Clays and Clay Minerals, 1972, Vol. 20, pp. 181–187. Pergamon Press. Printed in Great Britain

INTERLAMELLAR METAL COMPLEXES IN LAYER SILICATES III SILVER(I)–ARENE COMPLEXES IN SMECTITES

D. M. CLEMENTZ and M. M. MORTLAND
Department of Crop & Soil Sciences, Michigan State University, East Lansing, Mich. 48823, U.S.A.

(*Received* 24 *January* 1972)

Abstract–The complexation of benzene and several methyl substituted benzenes with exchangeable silver(I) on the interlamellar surfaces of Ag(I)–montmorillonite has been studied using spectroscopic methods. There are no physically adsorbed molecules interacting with the internal silicate surfaces and the only chemisorbed species present are those which are coordinated through π electrons to the exchangeable Ag(I) ions. In each case the coordinated species are similar to the previously studied Cu(II)–montmorillonite Type I complexes where aromaticity is retained. Complete replacement of coordinated and other interlamellar water molecules was accomplished with relative ease. Stoichiometric determinations indicate a 2:1 benzene:Ag(I) complex. Similarities between the Cu(II) and Ag(I) complexes are discussed in relation to electronic configurations.

INTRODUCTION

EXCHANGEABLE metal cations on the interlamellar surfaces of the swelling minerals such as the smectites have been shown to be capable of coordination with molecules which donate electrons. Obviously the complexation interaction depends upon the electron donating capabilities of the ligand and the electron accepting properties of the metal cation. Thus cations of the transition metal group having unfilled *d* orbitals possess relatively strong coordinating properties while the alkali metals are much less so inclined, alkaline earth metal ions being intermediate between these groups. Molecules possessing functional groups containing atoms such as N or O can form quite discrete complexes on the surface of the smectites if the exchangeable cation has strong electrophilic properties. In addition it has recently been shown that benzene (Doner and Mortland 1969, Mortland and Pinnavaia, 1971) and methyl substituted benzenes (Pinnavaia and Mortland, 1971) can complex with Cu(II) montmorillonite through donation of π electrons. The work here is concerned with π complexes between arenes and Ag(I) on the exchange sites of montmorillonite.

METHODS

Homoionic samples of the $< 2\mu$ fraction of Wyoming bentonite (A.P.I. H-25), and nontronite (A.P.I. H-33a) were prepared by washing the clay with $AgNO_3$ solution (1 N) and removing the excess nitrate by repeated washings with water until the conductivity of the supernatant liquid was negligible. The concentration of Ag(I) on the clay surface was determined by conductometric titration of freeze dried clay with standard HCl. Dispersed water suspensions of the clay were evaporated on a flat polyethylene surface and the clay films peeled away. Additional portions of the clay suspensions were evaporated on glass slides for X-ray analysis. The clay films and slides were placed in sealed chambers containing P_2O_5 and benzene vapor and equilibrated at 25°C for 2 hr. The thin films were then placed directly into the beam of the infrared spectrophotometer and the complete spectrum (600–4000)cm^{-1} recorded. In addition experiments were conducted where the clay film was placed in an evacuable brass cell fitted with NaCl windows and the spectra of the complexes obtained. The glass slides were placed directly into the X-ray diffractometer and scanned from 2–25° 2θ.

Ligand competition between benzene and water was studied by taking a thoroughly complexed Ag(I)–mont-benzene film and comparing the absorbence of the C–C stretching vibration (γ_{19}) of the complex (at 1471 cm^{-1}) to the deformation bands of water at 1620 cm^{-1}. Films initially saturated with benzene and a water content of zero were placed over a free water surface and the progress of ligand exchange monitored by periodically measuring the infrared absorbances.

Stoichiometry was determined using duplicate samples of Ag(I) montmorillonite following a method similar to that of Serratosa (1968). The films were dried over P_2O_5 for 24 hr and their mass determined to the nearest 0·1 mg. From these values the concentration of Ag(I) was calculated,

https://doi.org/10.1346/CCMN.1972.0200311 Published online by Cambridge University Press

using the predetermined value of exchangeable Ag(I) of 0·78 me/g for the clay. These films were then immersed in benzene and placed in a desiccator over P_2O_5. After 48 hr the films were taken out of the benzene and placed back into the desiccator. The system was evacuated with a vacuum pump for a period of 10 min to remove the benzene vapor and external physically adsorbed benzene. The amount of benzene in the complex was determined by immersing the films in measured volumes of methanol. Methanol replaces the benzene in the solid and dissolves it in the extracting liquid. After an equilibration time of 5 hr the concentration of benzene in the methanol solution was determined from its U.V. absorption at 254 mμ, using a standard benzene methanol curve. The completeness of replacement was verified by infrared examination of the films.

RESULTS

I.R. Figure 1 gives the i.r. absorption spectrum of the Ag(I) clay–benzene complex (spectrum B) as well as that of Ag(I)–clay (A). The complexed benzene has the C–C stretching vibration (ν_{19}) at 1471 cm^{-1} and the C–H out-of-plane vibration (ν_{11}) at 704 cm^{-1} while the band at 1845 cm^{-1} may be properly assigned to the ν_{17} and ν_{10} combination. This is about a 7 cm^{-1} shift toward low energy for the ν_{19} vibration and a 29 cm^{-1} shift toward the high energy for the ν_{11} vibration in comparison with the liquid form. These shifts are very similar to those of the type I Cu(II)–benzene–montmorillonite complexes reported earlier (Doner and Mortland, 1971; Pinnavaia and Mortland, 1971). They are also similar to those reported for benzene adsorbed on thin films of $AgClO_4$ (Karagounis and Peter, 1959). No evidence was found for a Ag(I)–benzene–montmorillonite complex like the type II Cu(II) complex where aromaticity is lost resulting in great changes in the spectrum of the benzene. Table 1 gives the C–C stretching (ν_{19}) and C–H out-of-plane (ν_{11}) vibrations for a number of arenes complexed with Ag(I) montmorillonite. Compared here are the ν_{19} and ν_{11} vibrations of liquid and physically adsorbed arenes with ligand arenes in Ag(I) montmorillonite. Table 2 compares the ν_{19} and ν_{11} vibrations of the Ag(I)–montmorillonite–arene complexes with those of the type I Cu(II)–montmorillonite systems. It is obvious that the magnitude of shifts for these two vibrations is very similar in the two types of complexes. It is interesting to note that only one species of adsorbed benzene is evident in the Ag(I)–clay (Fig. 1), that of the ligand form, while in the case of the Cu(II)–clay, bands associated with three forms of adsorbed benzene could be seen in one spectrum, physically adsorbed, type I, and type II ligand forms (Doner and Mortland, 1971; Pinnavaia and Mortland, 1971). This suggests that the benzene in the interlamellar regions of the Ag(I) montmorillonite is all in ligand form and that there is no room available for physically bound benzene that was so evident in the Cu(II) system. While

Table 1. The C–C (ν_{19}) and C–H (ν_{11}) Vibrations of several arenes in the liquid and physically adsorbed states and complexes with Ag(I)–montmorillonite

	C–C stretch (ν_{19})cm^{-1}			C–H out-of-plane (ν_{11})cm^{-1}		
Compound	Liquid	phys. adsorbed* on clay mineral	Ag(I) complex	Liquid	phys. adsorbed† on clay mineral	Ag(I) complex
Benzene	1478	1478	1471	675	688	704
Toluene	1495	1495	1487	728	738	756
o-xylene	1495	1495	1481	743	750	771
m-Xylene	1481	1481	1473	769	777	799
p-Xylene	1517	1517	1502	795	800	816
Mesitylene	1473	1473	1465	837	844	†
Ethyl-benzene	1499	1499	1487	745	755	780

*Taken from data of Pinnavaia and Mortland (1971).
†Obscured by vibrations of the silicate structure.

https://doi.org/10.1346/CCMN.1972.0200311 Published online by Cambridge University Press

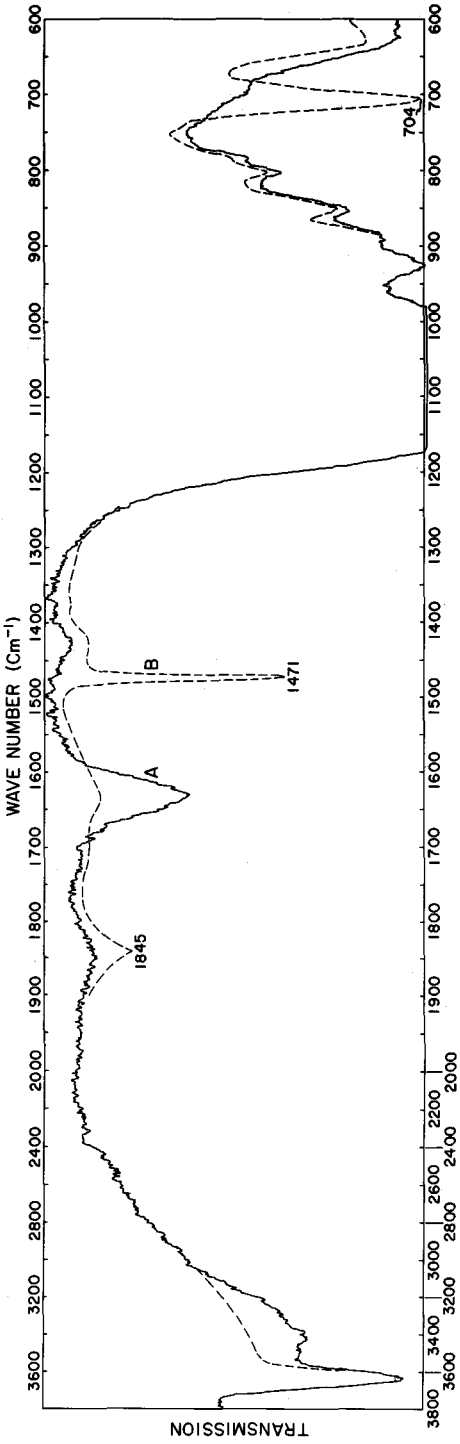


Fig. 1. I.R. spectra of Ag(I)–montmorillonite, air-dry film A, complexed with benzene B.

https://doi.org/10.1346/CCMN.1972.0200311 Published online by Cambridge University Press

Table 2. Changes in C–C (ν_{19}) and C–H (ν_{11}) vibrations of Cu(II) and Ag(I) montmorillonite arene complexes in comparison with the liquid state

Compound	$-\Delta$C–C(ν_{19})cm^{-1} Cu(II)	Ag(I)	$+\Delta$C–H(ν_{11})cm^{-1} Cu(II)	Ag(I)
Benzene	8(type I)	7	31(type I)	29
Toluene	8	8	36	28
o-Xylene	12	14	30	28
m-Xylene	8	8	34	30
p-Xylene	14	15	22	21
Mesitylene	10	8	53(?)	--

physically adsorbed benzene would be present on external surfaces, it would be immediately desorbed when the clay film was placed in the infrared beam.

X-ray diffraction. Table 3 gives the (001) spacing of a number of Ag(I)–montmorillonite–arene complexes. As indicated by the rationality of the higher orders, the spacings resulting from complex formation are quite discrete and homogeneous. The differences in spacing between the various complexes are explainable in terms of size of molecules as well are orientation within the interlamellar spaces. The (001) spacings of the xylene complexes are of particular interest in that the *o*-xylene complex has a 16·4 Å spacing while the other two isomers *p* and *m*-xylene have one of 15·2 Å. This highly significant difference in (001) spacing can likely be attributed to differences in molecular orientation.

Ligand competition. When maximum ligand formation has taken place, no water is in the interlamellar surfaces of the montmorillonite. Illustrating this is spectrum B in Fig. 1 where the benzene complex with Ag(I)–montmorillonite is shown indicating the absence of water by the lack of the H_2O deformation at 1630 cm^{-1}. It was noted with the Cu(II)–montmorillonite–benzene complexes, that no π complex was formed unless special procedures were taken to at least partially dehydrate the Cu(II). This dehydration was usually done with P_2O_5. On the other hand, the Ag(I)–complex with benzene could be formed merely by exposure to benzene vapor or by soaking the mineral film in liquid benzene. Obviously the benzene was in a better position for displacing any coordinated water from Ag(I) than from Cu(II). The inverse relationship between the amount of adsorbed water and adsorbed benzene is illustrated in Fig. 2 where a film of Ag(I)–montmorillonite–benzene complex was exposed to water vapor ($P/P_0 = 1$) and the absorbances of the ligand benzene at 1471 cm^{-1} and the water at 1630 cm^{-1} are plotted as water progressively displaced the ligand benzene from the system. When the absorbance of the ligand benzene was plotted against the square root of time a linear plot was obtained suggesting an obedience to the parabolic diffusion equation. The interdiffusion of both benzene and water probably determined the rate of displacement. These data prove that over a major portion of the competition experiment the water and benzene compete for the same adsorption sites in that in an environment where they are the only adsorbates, their concentrations in the mineral film are inversely linearly related. Undoubtedly at higher levels of water absorption other factors play an important role.

Table 3. (001) spacings (Å) of Ag(I)–montmorillonite-arene complexes calculated from various orders

Ligand	Order 001	002	003	004
Benzene	14·9	--	14·8	
Toluene	16·1	16·1	15·9	
o-Xylene	16·4	16·4	16·3	
p-Xylene	15·2		15·2	
m-Xylene	15·2		15·2	
Air dry Ag(I) montmorillonite	12·4			12·4

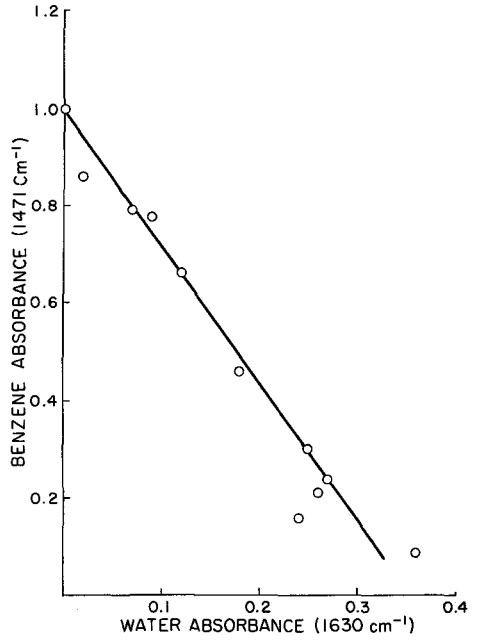


Fig. 2. Relationship of the i.r. absorbances of coordinated benzene (1471 cm^{-1}) and water (1630 cm^{-1}) on Ag(I)–montmorillonite.

https://doi.org/10.1346/CCMN.1972.0200311 Published online by Cambridge University Press

Stoichiometry. Since the adsorbed benzene was homogeneous being all in the ligand form as indicated in Fig. 1, it was possible to determine the proportions of benzene to Ag(I) in the montmorillonite. The exchangeable Ag(I) was determined by conductometric titration with standard HCl to be 78 me/100 g. The ratio of benzene/Ag(I) was found to be 1·82 and 2·18 in duplicate experiments. This obviously points to a 2:1 proportion of benzene to Ag(I). A number of benzene–Ag(I) complexes of that ratio have been reported in the literature (Beverwijk *et al.*, 1970).

DISCUSSION

The kinds of adsorbed benzene on the interlamellar surfaces of Cu(II) montmorillonite have been shown to be of three types: physical, and two species of ligand benzene types I and II (Doner and Mortland, 1969; Mortland and Pinnavaia, 1971; Pinnavaia and Mortland, 1971). In addition it was shown that alkyl substituted benzenes formed only two kinds, physical and the type I ligand (Pinnavaia and Mortland, 1971). The type I arene ligands are characterized by a low energy shift of the C–C stretching vibration (ν_{19}) of from 7 to 13 cm^{-1} and a high energy shift of the C–H out-of-plane vibration (ν_{11}) of from 22 to 36 cm^{-1} in comparison with the liquid state. The type II ligand of benzene however exhibits an infrared spectrum completely different from liquid benzene which indicates a loss of aromaticity and localization of electrons. The adsorption of benzene and alkyl substituted benzenes on Ag(I)–montmorillonite show very great similarities to the type I benzene and substituted benzenes on Cu(II)–montmorillonite as shown in Table 2, the amounts of shift of the ν_{19} and ν_{11} vibrations being very similar. No complex like the type II benzene–Cu(II)–montmorillonite was found. Another difference was that no physically adsorbed arenes were seen in the i.r. spectra. It thus appears that the arenes adsorbed in the interlamellar surfaces are all of the type I ligand form. Two reasons for this are possible; first there are twice as many Ag(I) as Cu(II) ions on the montmorillonite, thus doubling the possibilities for arene-metal interaction; second, the number of ligand arenes per Ag(I) ion may be greater than that for the Cu(II) ion. Since the Ag(I)–montmorillonite–benzene complexes were homogenous, accurate estimates of the benzene/Ag(I) ratio could be made and was found to be 2. It thus appears that once two benzene molecules are coordinated with each Ag(I) ion, no more room is available for physically adsorbed benzene. In the Cu(II) system however with half the number of metal ions, space was available for physically bound benzene after saturation of the ligand positions of the metal ion. The ligand benzene/Cu(II) ratio is still not known because of the various species of adsorbed benzene that are present.

For comparison of the similarities and differences between the benzene complexes of Cu(II) and Ag(I), examination of the electronic configurations of these ions is revealing. For a divalent copper ion, the electronic configuration of the outer orbitals is either $3d\,4s\,4p^2$ or $4s\,4p^2\,4d$ depending upon whether the unpaired electron is elevated to the $4p$ orbital or stays in the $3d$ orbitals. Both configurations are known to be energetically equivalent and capable of forming square planar bonding. The silver ion on the other hand has the $4d$ orbitals completely occupied leaving only the $5s$ and $5p$ orbitals available for electron donation from ligands which in four fold coordination leads to a tetrahedral configuration ($5s\,5p^3$). It might be possible if there were steric constraints, such as the layer structure of montmorillonite, that the silver ion might take on $5s\,5p^2\,5d$ configuration for a square planar arrangement as has been suggested for Zn(II) coordination with phtalocyanines (Kobayashi *et al.*, 1970), Zn(II) having a similar electronic configuration to Ag(I). The fact that Cu(II) montmorillonite forms the two kinds of benzene complexes (types I and II, see references) and the Ag(I) but one, suggests the possibility that since the type I Cu(II) and the Ag(I) complexes are very similar spectrally, that these are benzene ligands donating π electrons to the s and p orbitals forming "outer orbital" type complexes while the type II complex of the Cu(II) montmorillonite is an "inner orbital" type where the unpaired electron in the d orbitals is promoted to the p shell permitting acceptation of π electrons from benzene in the d orbitals of Cu(II). No such complex would be possible for Ag(I) which has the $4\,d$ orbitals completely occupied. Support for this view is found in the fact that Zn(II)– and Cd(II)–montmorillonite which are isoelectronic with Ag(I), make complexes with benzene somewhat similar spectrally to the Cu(II) type I and the Ag(I) (unpublished data). No benzene complexes of Ag(I), Zn(II), or Cd(II) were found that were like the Cu(II) type II system. If these are valid arguments then it seems that the Cu(II)–montmorillonite can form either "inner" (type II) or "outer" (type I) orbital complexes with benzene. It is realized that the above discussion is qualitative, however, it does permit an explanation for the observed behavior. For a more rigorous explanation one would have to know what effect the oxygen atoms or the electrical field imposed by the silicate surface have on the ligand field of the transition metal d electrons. To the authors'

https://doi.org/10.1346/CCMN.1972.0200311 Published online by Cambridge University Press

knowledge there is no such information available at this time. Since the type II species of arene–Cu(II)–montmorillonite complexes is limited to benzene (the alkyl substituted benzenes making only the type I, (Pinnavaia and Mortland, 1971), the presence of a substituent on the benzene ring must interfere with the donation of π electrons to the *d* orbitals of Cu(II).

Benzene forms complexes with silver salts in proportions of 1:1, 3:2, or 2:1 depending upon the nature of the anion (Beverwijk *et al.*, 1970). The 2:1 proportion found in the Ag(I)–montmorillonite thus falls within this group of silver salts. Alkyl substituted benzenes make complexes of 1:1, 2:1, or 3:1 proportions again depending upon the nature of the anion and the kind of substituted benzene involved. If it is assumed that the benzene ligands are inclined to the silicate surface at an angle of 45° (pleochroic studies indicate that it is inclined) and that the Ag(I) is bonded to the edge of the rings of two molecules (as in the silver salt complexes), the area covered by such an arrangement is about 110 $Å^2$ and explains the fact that only ligand benzene is found in the interlamellar surfaces, there being no room for additional benzene in the physically adsorbed condition in contrast to the Cu(II)–montmorillonite complexes where physically adsorbed benzene is quite evident.

It was reported earlier by Doner and Mortland (1969) that only octahedrally charged smectites made the complexes between exchangeable Cu(II) and the arenes. More recently Mortland (unpublished) was able to make the type I and II complexes on Cu(II)–nontronite but only after special pains were taken to dehydrate the system. As shown by Doner and Mortland (1971) the hydration of Cu(II) on the tetrahedrally charged smectites is much more energetic than in those of octahedral charge, thus the water is much more difficult to remove. Since one or more ligand positions must be uncovered on the exchangeable copper in order to make the arene complexes, this accounts for the difference in ease of arene complex formation. The Ag(I)–nontronite also made arene complexes, but much more easily than the Cu(II)–nontronite system since the energy of hydration of Ag(I) is so much less than that of Cu(II). However, it was more difficult to completely remove the H_2O of the Ag(I)–nontronite system than that of the Ag(I)–montmorillonite. Ag(I)–hectorite was also observed to make the arene complexes.

It is known that the silver ion will coordinate above and between two adjacent unsubstituted ring carbons when such positions are available. In fact the most favorable donor configuration for the silver complex formation is the one in which the alkyl substituents are packed together at adjacent carbon atoms of the ring (Mulliken, 1952). The X-ray data of Table 3 show that *o*-xylene gives the largest (001) spacing, with toluene being quite similar. This fact can be explained by Mulliken's concept if steric factors and intermolecular crowding in the regions of the interlamellar surface are considered. Toluene and *o*-xylene would be expected to be quite similar since Ag(I) complexation would be directed across the ring from the methyl groups and the effects would be less for the *p*- and *m*-xylenes as the substituted alkyl groups spread apart. Steric factors could cause all of the above mentioned substituted benzenes to have greater (001) spacings than benzene. This observation is further substantiated by pleochroic studies on the Ag(I)–montmorillonite complexes. Among the substituted benzene complexes only *o*-xylene, and to a somewhat lesser degree toluene, show an increase in intensity of the C–C stretching vibration (ν_{19}) when the clay film was changed from a right angle position to the incident i.r. beam to a 45°C position. The magnitudes of increase are roughly 50 and 25% respectively. This information indicates that these two species are more nearly vertical in their location between the plates than benzene and the other substituted benzenes, which apparently are tilted at an angle closer to 45°C.

Acknowledgment—Published with the approval of the Michigan Agricultural Experiment Station Journal Article No. 5818.

REFERENCES

Beverwijk, C. D. M., Van Der Kerk, G. J. M., Leusink, A. J. and Noltes, J. G. (1970) Organosilver chemistry: In *Organometallic Chemistry Reviews* A 215–280.

Doner, H. D. and Mortland, M. M. (1969) Benzene complexes with Cu(II)–montmorillonite: *Science* **166**; 1406–1407.

Doner, H. E. and Mortland, M. M. (1971) Charge location as a factor in the dehydration of 2:1 clay minerals: *Soil Sci. Soc. Am. Proc.* **35**, 360–361.

Karagounis, V. G. and Peter, O. V. (1959) Über das Infrarotspektrum Organischer Verbindungen gespreitet in dünnen schichten auf Oberflachen von lonengittern: *Z. Electrochem.* **63**, 1120.

Kobayashi, T., Kurokawa, F., Uyeda, N. and Suito, E. (1970) The metal–ligand vibrations in the infrared spectra of various metal phthalocyanines: *Spectrochimica Acta* **26A**, 1305–1311.

Mortland, M. M. and Pinnavaia, T. J. (1971) Formation of copper(II) arene complexes on the interlamellar surfaces of montmorillonite: *Nature (Physical Science)* **229**, 75–77.

Mulliken, R. S. (1952) Molecular compounds and their spectra: *J. Am. Chem. Soc.* **74**, 811–824.

https://doi.org/10.1346/CCMN.1972.0200311 Published online by Cambridge University Press

Pinnavaia, T. J. and Mortland, M. M. (1971) Interlamellar metal complexes on layer silicates I Cu(II)–arene complexes on montmorillonite: *J. Phys. Chem.* **75**, 3957–3962.

Serratosa, J. M. (1968) I.R. study of benzonitrile (C_6H_5CN)–montmorillonite complexes: *Am. Mineralogist* **53**, 1244–1251.

Résumé – On a étudié au moyen de méthodes spectroscopiques le complexage du benzène et de plusieurs benzènes méthyl substitués par l'argent (I) échangeable sur les surfaces interlamellaires de montmorillonite Ag (I). Il n'y a pas de molécules adsorbées physiquement en interaction avec les surface internes du silicate et les seules espèces chimisorbées présentes sont celles qui sont coordonnées par les électrons π aux ions Ag (I) échangeables. Dans tous les cas les espèces coordonnées sont semblables aux complexes du type I Cu (II)-montmorillonite étudiés dans un travail antérieur, et dans lesquels le caractère aromatique est conservé. Il est relativement facile de remplacer complètement les molécules d'eau coordonnées et les autres types de molécules d'eau interfeuillet. Les déterminations concernant la stoechiométrie indiquent qu'il s'agit d'un complexe benzène: 2–Ag (I): 1. Les similitudes existant entre les complexes avec Cu (II) et Ag (I) sont discutées sur la base des configurations électroniques.

Kurzreferat – Die Komplexbildungv von Benzol und verschiedenen methyl-substituierten Benzolen mit austauschbarem Silber (I) an den zwischenschichtigen Oberflächen von Ag (I)–Montmorillonit wurde untersucht unter Verwendung spektroskopischer Methoden. Physikalisch adsorbierte Moleküle reagieren nicht mit den inneren Silikatoberflächen und die einzigen chemisch sorbierten Sorten sind die durch π-Elektronen mit den austauschbaren Ag (I) Ionen koordinierten Stoffe. In allen Fällen sind die koordinierten Materiale ähnlich den früher untersuchten Cu (II)–Montmorillonit Typ I Komplexen woder aromatische Charakter erhalten blieb. Ein vollständiger Ersatz koordinierter und anderer zwischenschichtiger Wassermoleküle konnte verhältnismässig leicht erzielt werden. Stöchiometrische Bestimmungen zeigen einen 2:1 Benzol: Ag (I) Komplex an. Es werden Ähnlichkeiten zwischen Cu (II) und Ag (I) Komplexen in bezug auf Elektronenanordnungen erörtert.

Резюме — Образование комплексов бензола и нескольких замещенных метилом бензолов с обменным серебром (I) на межслойных поверхностях Ag(I)–монтмориллонит изучалось методом спектроскопии. Физически адсорбированных молекул, взаимодействующих с внутренними поверхностями силикатов, не имеется; единственными хемосорбированными видами являются виды, координационные через π-электроны с замещаемыми ионами Ag(I). В каждом случае координационные виды подобны изучаемому раньше типу I Cu(II)–монтмориллонит комплекса, где степень ароматизации удерживается. Полное замещение координационных и других межслойных молекул воды было достигнуто сравнительно легко. Стехиометрические определения показали комплекс 2:1 бензол: Ag(1). Обсуждается подобие комплексов Cu(II) и Ag(I) в отношении электронных конфигураций.

https://doi.org/10.1346/CCMN.1972.0200311 Published online by Cambridge University Press