THE CHEMISORPTION OF ANISOLE ON Cu(II) HECTORITE*

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Abstract—The sorption of anisole and some related aromatic ethers on the interlamellar surfaces of Cu(II) hectorite has been investigated by i.r. and e.s.r. spectroscopy. In addition to physical adsorption, anisole forms two distinct types of Cu(II) complexes which are analogous to the type I and II species previously reported for benzene–Cu(II) smectite systems. These complexes can be transformed to type I and II complexes of 4,4′-dimethoxybiphenyl. Possible mechanisms are proposed for the oxidation process. Butyl phenyl ether formed a type II complex with Cu(II)–hectorite, but no dimerization reaction was noted in this system. Phenyl ether and benzyl methyl ether form a type I π complex with Cu(II)–hectorite. No type II analog was noted. E.S.R. spectra of each of the type II ether–Cu(II)–hectorite systems showed a single, narrow band with g near the value expected for a "free spinning" electron. The type I phenyl ether and benzyl methyl ether complexes also exhibited this e.s.r. band. Ag(I) hectorite adsorbs anisole by forming exclusively a type I complex. Na(I) and Co(II) hectorite adsorb anisole by physical means only, indicating association with the silicate surface.

INTRODUCTION

SEVERAL recent studies have shown that a variety of aromatic molecules are chemisorbed on the interlamellar surfaces of copper(II) exchange forms of smectite minerals via complex formation with the metal ion. Doner and Mortland (1969) and Mortland and Pinnavaia (1971) found that two distinct types of complexes are formed with benzene: a type I species in which the copper(II) ion is edge bonded to the benzene and aromaticity is retained, and a type II species in which the benzene ring is believed to be distorted with some localization of the C=C bonds. Phenol and alkyl substituted benzenes (Fenn and Mortland, 1972; Pinnavaia and Mortland, 1971) can also complex with Cu(II) via donation of π electrons, although only type I analogs are observed. More recently, Rupert (1973) has shown that type II complex formation is not unique to benzene, but that analogous species can be formed with aromatic molecules containing two or more benzene rings.

Silver(I) ions will coordinate to aromatic molecules on the interlamellar surfaces of clay minerals (Clementz and Mortland, 1972) but in all of the Ag(I)–arene systems investigated only type I complexes were observed.

The present paper reports some spectroscopic studies of the chemisorption of anisole on Cu(II) hectorite. In addition to the formation of type I and type II complexes an interesting redox reaction occurs in this system. The behavior of related aromatic ether–metal ion systems is also reported.

MATERIALS AND METHODS

Homoionic hectorite preparation

The hectorite (B1-26), one of the smectite (montmorillonitic) type of clay minerals, used in this study was obtained from the Baroid Division of NL Industries, Inc. The unit cell formula is $M_{0.42}^+[Mg_{5.42}Li_{0.68}Al_{0.02}](Si_{8.00})O_{20}(F, OH)_4$. Homoionic samples of the $<2\,\mu$m fraction were prepared by washing the clay mineral three times with a 1 N chloride salt solution of the desired cation and then removing the excess salt by dialysis until the $AgNO_3$ test for Cl^- was negative. Ag(I)–hectorite was prepared as above from a 1 N nitrate salt solution. Thin, self-supporting films of the homoionic mineral were then formed by depositing a few milliliters of suspension on a polyethylene sheet, allowing it to air dry, and then carefully peeling away the clay film. Films prepared in this manner are highly oriented, with the silicate sheets lying parallel to the film surface.

Clay–organic complexation

The homoionic clays were allowed to adsorb the

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anisole or other aromatic ether by placing the clay film in a desiccator containing P_2O_5 and a few g of the ether. At least 24 hr of equilibration time were allowed before any determinations were made on the film.

I.R. Spectra

I.R. spectra in the region 4000–600 cm^{-1} were obtained on a Beckman I.R.-7 spectrophotometer. After exposure to the aromatic ether, the clay film was mounted in a special brass cell fitted with a heating element, vacuum stopcock and NaCl windows to exclude atmospheric moisture while the spectra were being obtained.
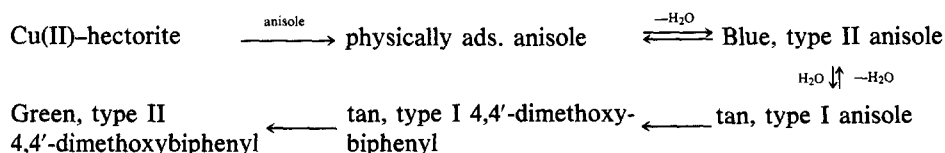
The highly ordered nature of the clay film allows one to investigate pleochroic effects by observing absorption intensities of certain bands when the clay film is positioned at 45 and 90° with respect to the infrared beam. By this technique it is possible to determine the orientation of the adsorbed species relative to the clay mineral layers.

E.S.R. Spectra

E.S.R.-band spectra were obtained with a Varian not allowed to age for more than a few minutes at room temperature. Prolonged aging results in the formation of a tan type I 4,4′-dimethoxybiphenyl complex and, eventually, a green type II 4,4′-dimethoxybiphenyl complex. The rate at which the tan species is transformed to the green complex is dependent on the concentration of adsorbed water. In the presence of liquid water the tan complex is stable indefinitely, whereas at lower relative humidities it transforms to the green complex within a few hours. The dependence on water concentration is attributed to a surface acidity effect. It is known that the acidity of a clay surface is greatest at low water concentrations due to extensive hydrolysis of the exchangeable metal ion. At high water concentrations the extent of hydrolysis is greatly reduced. The importance of surface acidity was confirmed by observing an almost instantaneous transformation of the blue anisole complex to the green 4,4′-dimethoxybiphenyl complex when the former was exposed to HCl vapors.

The processes occurring in the anisole–Cu(II)–hectorite system can be summarized as follows:

$$\text{Cu(II)–hectorite} \xrightarrow{\text{anisole}} \text{physically ads. anisole} \underset{\xrightarrow{\hspace{1cm}}}{\overset{-H_2O}{\longleftarrow}} \text{Blue, type II anisole}$$

$$H_2O \updownarrow \; -H_2O$$

$$\underset{\text{4,4′-dimethoxybiphenyl}}{\text{Green, type II}} \xleftarrow{\hspace{1cm}} \underset{\text{biphenyl}}{\text{tan, type I 4,4′-dimethoxy-}} \xleftarrow{\hspace{1cm}} \text{tan, type I anisole}$$

E-4 spectrometer. The spectra of randomly oriented samples of complexes of the homoionic clays were obtained by exposing freeze dried clay samples to the aromatic ether vapors in the presence of P_2O_5 desiccant, and then introducing the complex into an e.s.r. tube.

Values of g were determined from the spectrometer frequency and the magnetic field strength at the center of the first derivative signal.

RESULTS AND DISCUSSION

Anisole adsorbed by Cu(II) hectorite under ambient conditions is physically bound to the clay surfaces. In the presence of P_2O_5, however, anisole replaces water at the coordination sites on copper(II) and a dark blue type II complex readily forms. Exposure of the blue complex to atmospheric moisture results initially in the formation of tan type I anisole complex and physically adsorbed anisole. Upon desiccation over P_2O_5, the tan anisole complex reforms the blue type II complex.

The interconversion of the blue and tan anisole complexes is possible only if the latter complex is

After extraction with hot methanol, the chemisorbed aromatic molecules were identified by comparing their u.v. (anisole) or i.r., h.n.m.r., and mass spectra (4,4′-dimethoxybiphenyl) with those of authentic samples. The assignment of type I and type II complexes in the above scheme is based on the following i.r. absorption data.

The i.r. spectrum of liquid anisole is shown in Fig. 1a, and the spectrum of a thin Cu(II)–hectorite film, which possessed the pale blue color characteristic of hydrated Cu^{2+}, is shown in Fig. 1b. The infrared absorption bands of anisole adsorbed on Cu(II) hectorite under ambient conditions (Fig. 1c) correspond closely to those of liquid anisole, indicating that this form of adsorbed anisole is only physically bound to the clay mineral structure. Anisole is unable to compete favorably with water for ligand positions on the cation, and the pale blue color of the clay is retained.

The spectrum of the blue anisole complex (Fig. 1e) bears little resemblance to the spectrum of liquid anisole (Fig. 1a) and is clearly a type II analog. The very intense absorption above
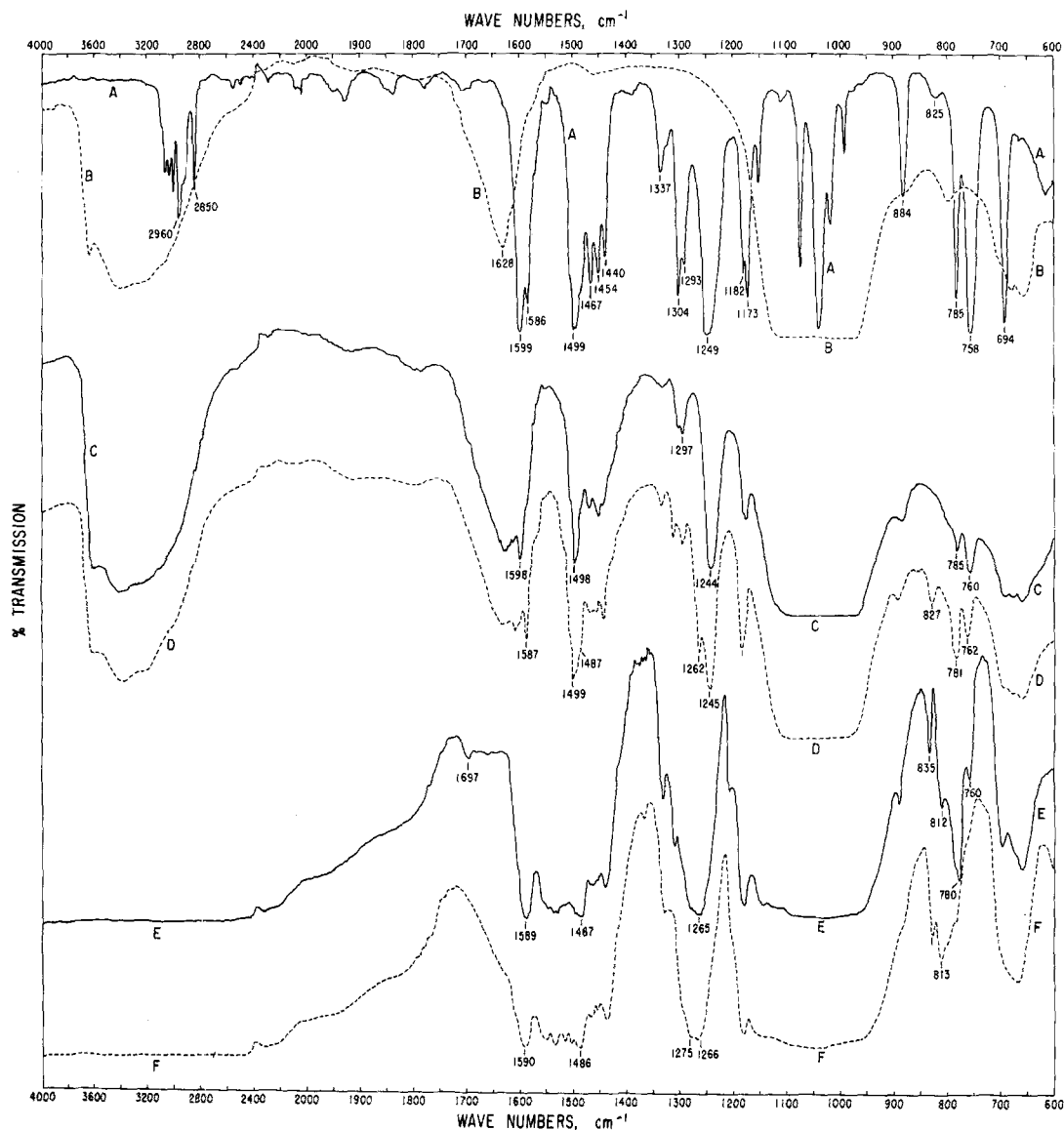
Fig. 1. I.R. spectra of (a) liquid anisole, (b) air dry Cu(II)–hectorite film, (c) physically bound anisole on Cu(II)–hectorite, (d) type I (tan) anisole complex on Cu(II)–hectorite, (e) type II (blue) anisole complex on Cu(II)–hectorite, and (f) type II (green) 4,4'-dimethoxybiphenyl complex on Cu(II)–hectorite.

$1800 \, \text{cm}^{-1}$ corresponds directly with that of the type II benzene complex, which Mortland and Pinnavaia (1971) attribute to a low energy electron transition arising from the d-π Cu(II)–benzene interaction. The CH out-of-plane region of liquid anisole, Fig. 1a, shows a band at $758 \, \text{cm}^{-1}$. In Fig. 1e we find a band at $760 \, \text{cm}^{-1}$ corresponding to physically sorbed anisole, a strong band at $780 \, \text{cm}^{-1}$ which is attributed to a type I complex, and a band at $812 \, \text{cm}^{-1}$ which is attributed to the CH out-of-plane vibration characteristic of the type II anisole com-

plex. This latter position represents about a $60 \, \text{cm}^{-1}$ high energy shift of the CH out-of-plane mode upon type II complexation. The C–C stretching region of liquid anisole shows several clearly defined bands and shoulders. Formation of the type II complex produced shifts in the energies of these bands which overlap with absorption bands of the other two forms of adsorbed anisole present, creating the broad adsorption region found between 1400 and $1600 \, \text{cm}^{-1}$.

The presence of an intense band in the i.r. region

above $1600\ cm^{-1}$ and a high energy CH deformation at $813\ cm^{-1}$ in the spectrum of the green 4,4'-dimethoxybiphenyl complex (Fig. 1f) indicates that this complex is also a type II species, analogous to the blue anisole complex.

The spectrum of the tan anisole complex, Fig. 1d, indicates it to be a type I analog. There is no indication of the broad intense adsorption above $1800\ cm^{-1}$ as in the type II spectrum of benzene (Doner and Mortland, 1969), but the CH out-of-plane vibration is shifted up $23\ cm^{-1}$ compared to liquid anisole. The ν_{16} C–C stretching vibration has been shifted down $11\ cm^{-1}$ to $1587\ cm^{-1}$, and a new band appears at $1262\ cm^{-1}$. This latter band likely arises from a $13\ cm^{-1}$ high energy shift of the C–O–CH₃ stretching mode upon formation of the type I complex.

If a tan type I complexed film is not put in the infrared cell, but mounted directly in the infrared beam, it will shortly turn bluish and exhibit the type II anisole spectrum. The heat of the infrared beam is evidently enough to partially dehydrate the film and convert the type I to the type II anisole complex. A similar effect was noted with the biphenyl–Cu(II)–montmorillonite complex (Rupert,

1973). If the film is removed from the infrared beam it comes tan once again. Table 1 contains the assignments of the infrared bands for the three forms of adsorbed anisole.

Pleochroic studies on the type II anisole complex showed no changes in intensity of any of the in-plane or out-of-plane vibrational modes, a result which suggests that the anisole is lying in the inter-lamellar regions near an angle of 45° to the clay plates.

Stoichiometric studies on the type II system indicated that a total of about 5 molecules of anisole are adsorbed per exchangeable Cu^{2+} ion on the hectorite. Since the clay-organic system also contained physically sorbed and type I anisole molecules, it is difficult to assign a given proportion of ligand anisole per copper ion.

The adsorption of anisole on other kinds of homoionic hectorite was also studied. Fig. 2 shows representative spectra from this study. As can be seen in Fig. 2a, the Ag(I)–hectorite formed a type I complex with anisole. The CH out-of-plane band at $780\ cm^{-1}$, the C–O–CH₃ mode at $1262\ cm^{-1}$, and the C–C stretches at $1487\ cm^{-1}$ and 1587^{-1} all correspond to the type I Cu(II)–anisole complex bands in
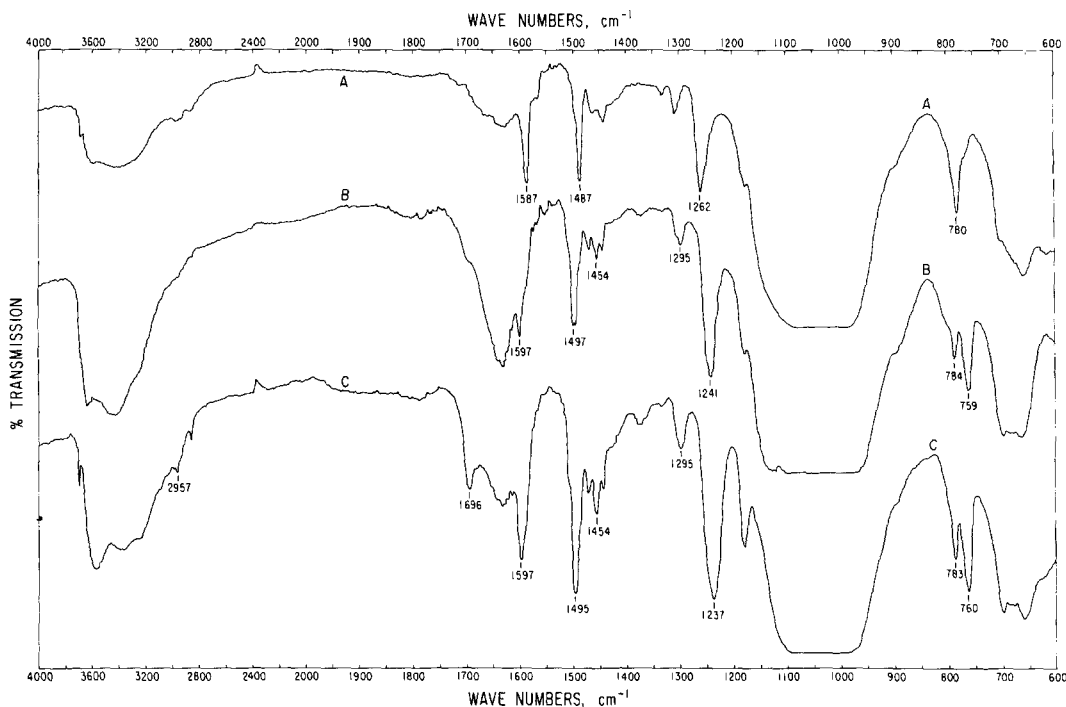

Fig. 2. I. R. spectra of anisole on (a) Ag(I)–hectorite, (b) Na⁺–hectorite and (c) Co(II–hectorite. In each case the anisole was adsorbed in the presence of P_2O_5 as a desiccant.

Fig. 1d. As was noted in previous studies on Ag(I)–hectorite–arene complexes (Clementz and Mortland, 1972; Fenn and Mortland, 1972) no physically bound anisole was adsorbed on the Ag(I)–hectorite. Twice as many Ag(I) ions are needed to satisfy the hectorite exchange capacity than Cu(II) ions. The formation of the type I complex by anisole molecules on Ag (I)–hectorite effectively covered the interlamellar surface area and blocked the physical adsorption sites on the silicate structure, although there is evidence in Fig. 2a of readsorption of some water when the film was exposed to the atmosphere.

As shown in Fig. 2b and c, both Na^+–hectorite and Co(II)–hectorite adsorbed anisole by physical means only. The adsorption process appears to be independent of the exchangeable cation since similar spectra were obtained for all the kinds of homoionic hectorite studied where physically sorbed anisole was present. The band at $1696\ cm^{-1}$ in Fig. 1e and 2c however, appears only in the transition metal saturated hectorite but not in the alkali metal or alkaline earth saturated hectorite studied. The band is in the C=O stretching region, but there is no other indication of ketone or quinone formation from anisole. The origin of this weak band cannot yet be explained and requires further study.

The most interesting feature of the adsorption of anisole on Cu(II)–hectorite is its oxidation to 4,4'-dimethoxybiphenyl. Two mechanisms can be proposed. One pathway, similar to that suggested by Kovacic and Kyriakis (1962) for the oxidation of benzene by copper(II) in the presence of $AlCl_3$ and water, involves a carbonium ion intermediate:
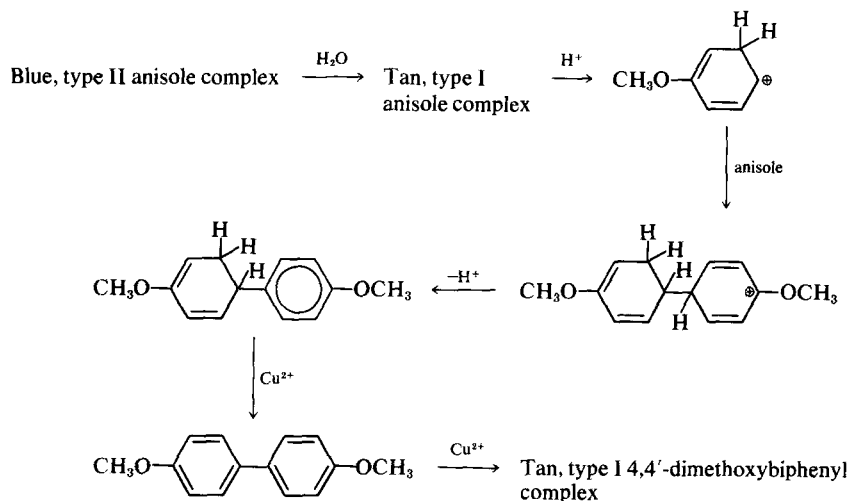
The second possible mechanism proceeds through a radical cation:

Tan, type I
4,4'-dimethoxybiphenyl complex.

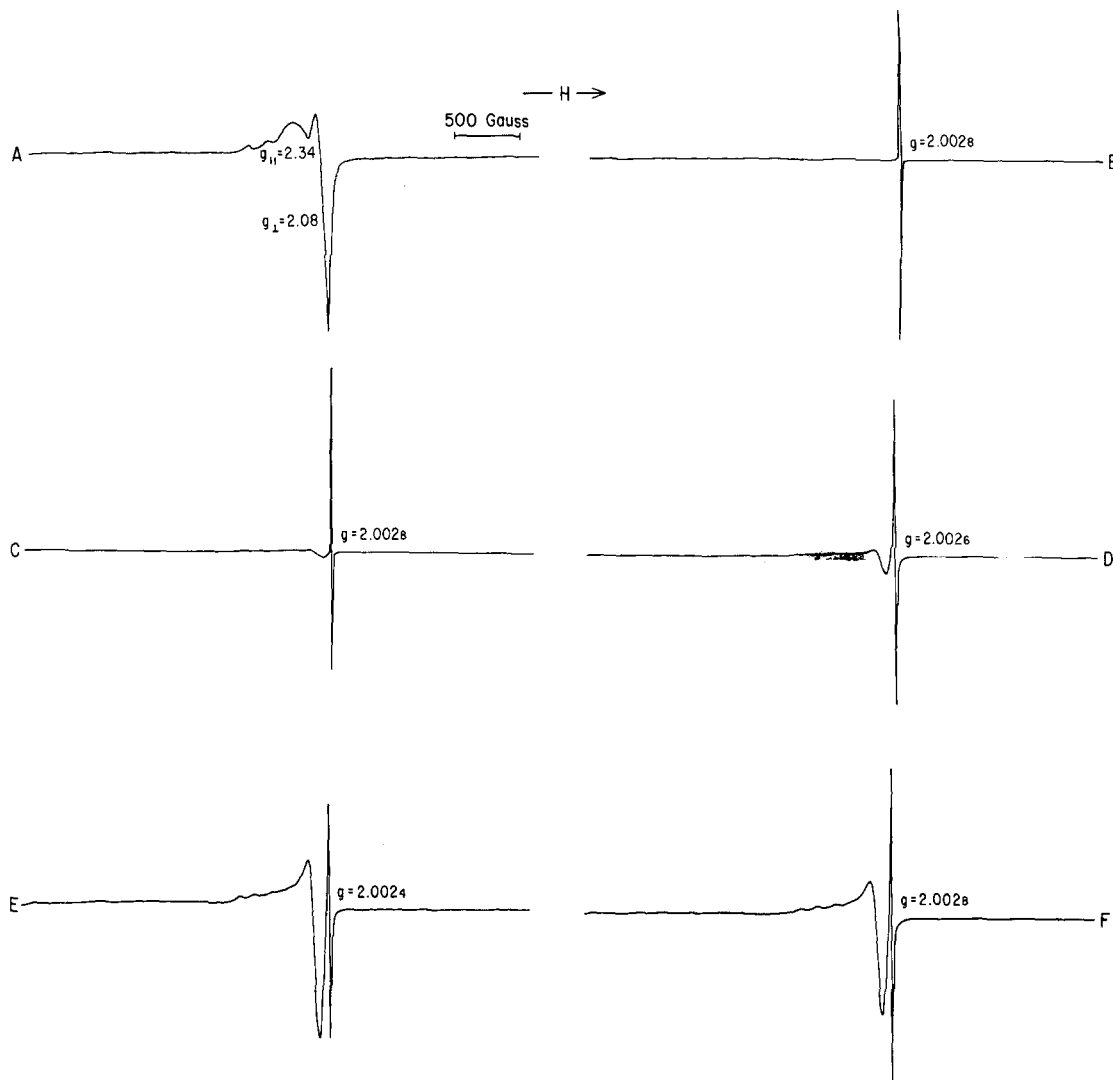320   D. B. Fenn, M. M. Mortland and Thomas J. Pinnavaia
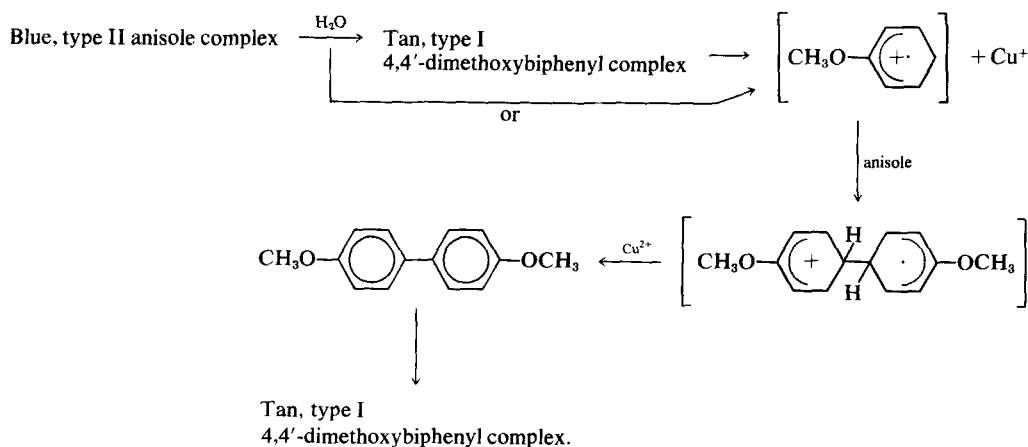
Fig. 3. E.S.R. spectra of (a) air-dried Cu(II)–hectorite, (b) blue, type II anisole complex (c) green, type II 4,4'-dimethoxybiphenyl complex, (d) purple, type II butyl phenyl ether complex (e) brown, type I benzyl methyl ether and (f) green, type I phenyl ether complex.

The marked increase in the rate at which the blue anisole complex is converted to the green 4,4'-dimethoxybiphenyl complex in the presence of HCl tends to support the carbonium ion pathway. However, this pathway is unattractive as it requires protonation of the anisole ring at the meta position rather than the more favorable ortho or para positions. No 2,3'- or 3,4'-dimethoxybiphenyl is observed as a reaction product. The role of the acid may be to facilitate the reoxidation of Cu(I) to the Cu(II) needed to form the green 4,4'-dimethoxybiphenyl complex.

Electron spin resonance spectra of the type II blue anisole and green 4,4'-dimethoxybiphenyl complexes along with the spectrum of air-dried Cu(II)–hectorite are shown in Figs. 3b, c, and a. The latter spectrum has been interpreted recently by Clementz, Pinnavaia, and Mortland (1973). Both complexes exhibit a single, sharp signal with g very near the value of $2 \cdot 0023$ for a free electron. The tan, type I 4,4'-dimethoxybiphenyl complex exhibits only an isotropic Cu^{2+} e.s.r. signal. The absence of hyperfine structure for the type II complexes is attributed to rapid electron processes. Rupert (1973) has recently observed completely analogous spectra for type II complexes of benzene and other

Table 1. Assignments of selected vibrational frequencies (cm^{-1}) of anisole as a liquid, as a physically bound species on all homoionic hectorites studied, as a type I ligand on Cu(II)–hectorite, and a type II ligand on Cu(II)–hectorite.

Liquid	Physically bound	Type I Cu(II)	Type II Cu(II)	Assignment
690	696		699	δ C–C (ν_8)*
752	760	781	812	ν C–H (ν_4)
783	785			ν C–O–CH$_3$ (ν_2)
825		827	835	ν C–H (ν_{11})
880	885	885	890	ν C–H ($\nu_{11'}$)
1180	1178	1182	1180	methyl bending?
1247	1244	1262	1265	ν C–O–CH$_3$ (ν_{12})
1292	1297	1294	1280	β C–H (ν_3)
1304	1305	1313	1312	methyl bending
1332		1335	1333	ν C–C (ν_9)
1442	1445	1442	1440	?
1454	1454	1454	†	ν C–C ($\nu_{13'}$)
1469	1470	1470	†	methyl bending
1499	1498	1487	†	ν C–C (ν_{13})
1588			†	ν C–C ($\nu_{16'}$)
1599	1598	1587	1589	ν C–C (ν_{16})

*Assignments for liquid anisole taken from Green (1961) and Stephenson, Coburn and Wilcox (1961).

†Broad overlapping of bands makes assignment difficult.

aromatic molecules on a copper(II) exchange form of montmorillonite and has suggested possible electron exchange mechanisms.

Experiments were performed with benzyl methyl ether on Cu(II)–hectorite for comparison with the anisole system. In anisole, electrons on the ether oxygen are likely involved with the electronic system of the aromatic ring, while in benzyl methyl ether, the oxygen is removed from the aromatic ring by a CH$_2$ group which prevents the oxygen from participating in resonance. The benzyl methyl ether formed a type I complex as evidenced by shifts in CH out-of-plane and C–C stretching vibrations but no type II formed. This result is completely analogous to the results obtained by Pinnavaia and Mortland (1971) with alkyl substituted arenes on Cu(II)–montmorillonite where only type I complexes were formed. Resonance interactions between the ring and the ether oxygen of anisole and of 4,4'-dimethoxybiphenyl therefore appear to be critical in the formation of the type II complexes of those compounds. Butyl phenyl ether, analogous to anisole, formed a type II complex with Cu(II)–hectorite, while biphenyl ether formed only a type I species.

The e.s.r. spectra for the type II butyl phenyl ether and the type I biphenyl ether and benzyl methyl ether complexes on Cu(II)–hectorite are shown in Fig. 3d, e, and f. Type II complexes show the typical free spinning electron signal. However, the type I benzyl methyl ether and phenyl ether complexes also exhibit this signal. These appear to be the first examples of type I complexes exhibiting a "free" electron signal.

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Résumé—La sorption de l'anisole et de certains éthers aromatiques voisins par les surfaces interlamellaires de l'hectorite Cu(II) a été étudiée par spectroscopie infrarouge et résonance de spin électronique. En plus de l'adsorption physique, l'anisole forme deux types distincts de complexes Cu(II) que sont analogues aux types I et II précédemment signalés dans le cas des systèmes benzène–

smectite Cu(II). Ces complexes peuvent être transformés en les types I et II des complexes du 4-4' dimethoxybiphenyl. Des mécanismes possibles sont proposés pour le processus d'oxydation. Le butyl phenyl éther forme un complexe du type II avec l'hectorite Cu(II), mais aucune réaction de dimérisation n'est notée dans ce système. Le phenyl éther et le benzyl methyl éther forment un complexe π du type I avec l'hectorite Cu(II). Aucun analogue du type II n'est noté. Les spectres de RSE de chacun des systèmes éther–hectorite Cu(II) du type II montrent une bande unique et étroite avec g voisin de la valeur attendue pour un électron à "spin indifférent". Les complexes du type I obtenus avec le phenyl éther et le benzyl methyl éther montrent également cette bande en RSE. L'hectorite Ag(I) adsorbe l'anisole en formant exclusivement un complexe du type I. Les hectorites Na(I) et Co(II) adsorbent l'anisole par voie physique seulement, ce qui indique une association avec la surface du silicate.

Kurzreferat—Die Sorption von Anisol und einigen verwandten aromatischen Äthern an den Zwischenschichtoberflächen von Cu(II)—Hectorit wurde mit Infrarot—und Elektronenspinresonanz Spektroskopie untersucht. Zusätzlich zur physikalischen Adsorption bildet Anisol zwei verschiedene Typen von Cu(II)—Komplexen, die den früher für Benzol–Cu(II)–Smectit–Systeme beschriebenen Typen I und II analog sind. Diese Komplexe können in Typ I– und II–Komplexe von 4,4'–Dimethoxydiphenyl umgewandelt werden. Mögliche Mechanismen für den Oxidationsprozeß werden vorgeschlagen. Butylphenyläther bildet einen Typ II–Komplex mit Cu(II)–Hectorit, jedoch wurde in diesem System keine Dimerisationsreaktion festgestellt. Phenyläther und Benzylmethyläther bilden mit Cu(II)–Hectorit einen Typ I–ß-komplex. Analoge Type II–Komplexe wurden nicht gefunden. ESR–Spektren von jedem der Typ II–Äther–Cu(II)–Hectorit–Systeme zeigten ein einzelnes, schmales Band mit g nahe dem Wert, der für ein Elektron mit "freiem Spin" zu erwarten ist. Phenyläther– und Benzylmethylätherkomplexe vom Typ I wiesen ebenfalls dieses e.s.r.-Band auf. Ag(I)-Hectorit adsorbiert Anisol ausschließlich durch Bildung von Typ I–Komplexen. Na(I)– und Co(II)–Hectorit sorbieren Anisol nur auf physikalischem Wege, was auf eine Bindung an die Silikatoberfläche hinweist.

Резюме — Сорбция анизола и некоторых родственных простых эфиров ароматического ряда на межпластинчатых поверхностях Cu(II)-гекторита изучалось инфракрасной и электронной спиновой резонансной спектроскопией. Добавочно к физической адсорбции, анизол образует два обособленных типа комплексных соединений Cu(II), которые аналогичны группам I и II как ранее сообщалось для систем бензол-Cu(II) смектитов. Эти комплексные соединения можно перегруппировать в комплексные соединения типа I и II 4,4'-диметоксидифенила. Выдвигаются возможные механизмы процесса окисления. Бутилфеноловый эфир с Cu(II)-гекторитом образует комплексное соединение типа II, но в этой системе не замечается реакция димеризации. Феноловый и бензилодиметиловый эфиры с Cu(II)-гекторитом образуют комплексное соединение типа I п. Аналог типа II не был замечен. Спектр электронного спинового резонанса каждого типа системы эфира-Cu(II)-гекторита показал одну узкую полосу, с g приближающимся к значению ожидаемого от «свободно вращающегося относительно своей оси» электрона. Комплексные соединения фенолового и бензилодиметилового эфиров типа I также проявляют эту полосу электронного спинового резонанса. Ag(I) гекторит адсорбирует анизол образуя исключительно сложное соединение типа I. Na(I) и Co(II) гекторит адсорбирует анизол только физическим способом, что указывает на ассоциацию с силикатной поверхностью.