

Pyridinium-Montmorillonite Complexes with Ethyl

N,N-Di-*n*-propylthiolcarbamate (EPTC)

The presence of an organic cation (pyridinium) on the exchange complex of montmorillonite facilitates the adsorption of a herbicide, ethyl *N,N*-di-*n*-propylthiolcarbamate (EPTC). The stability of the complex formed is higher than that formed by clay with exchangeable metal ions. The complex is characterized by a 1-to-1 ratio of pyridinium to

EPTC and probably results from a hydrogen bond between the protonated nitrogen of pyridinium and the carbonyl of EPTC. This model system suggests that organic compounds in soil organic matter upon interaction with clay may facilitate and stabilize adsorption of pesticides beyond that observed in a purely inorganic clay system.

Pyridinium-montmorillonite forms relatively stable complexes with other organic compounds, such as benzene (Farmer and Mortland, 1966) and chlorobenzene (Serratosa, 1968). Complexes of ethyl *N,N*-di-*n*-propylthiolcarbamate (EPTC) with montmorillonite (Mortland and Meggitt, 1966), are greatly influenced by the nature of the exchangeable metal cation. Infrared absorption data indicate that a major mechanism of bonding involves ion-dipole interaction between the exchangeable metal ion and the carbonyl group of the EPTC. Therefore, the author thought that the presence of an organic cation on the exchange complex might facilitate the adsorption of organic pesticides in the same manner as for benzene and chlorobenzene. The resulting complex might have different properties than those present when metal cations saturate the exchange complex. Studies were then made on the complex formed between pyridinium-montmorillonite and EPTC from the standpoint of its nature and stability.

Pyridinium-montmorillonite was prepared by treating the sodium-saturated clay fraction of Wyoming montmorillonite from Upton (Reference Clay Mineral No. 25, Ward, Rochester, N.Y.) with an excess of pyridinium chloride. The sample was washed with distilled water until no chloride appeared in the washings upon testing with silver nitrate. Thin self-supporting clay films (2 mg. per sq. cm.) were prepared by evaporation of the water suspension in aluminum foil dishes covered with polyethylene plastic. The films were then immersed in pure liquid EPTC for 3 days. The films had a transparent appearance while in the EPTC, an effect which persisted upon removal of the films from the liquid until much of the liquid EPTC had evaporated. The clay films with the adsorbed EPTC were placed at right angles to the beam in an infrared spectrophotometer (IR-7) and spectra were obtained. The 001 spacings of the clay-organic systems were obtained with a Philips x-ray diffractometer using filtered copper radiation.

DISCUSSION OF RESULTS

Some of the absorption frequencies for pyridinium-montmorillonite, pyridinium-EPTC-montmorillonite complex, and liquid EPTC are given in Table I. Figure 1 shows the infrared spectra of pyridinium-montmorillonite (dashed lines) and pyridinium-EPTC-montmorillonite (solid lines). The appearance of the C—O stretching frequency of the EPTC at 1597 cm^{-1} and the C—N stretching frequency at 1227 cm^{-1} in the clay complex is comparable with the complexes of EPTC with montmorillonite saturated with metallic cations (Mortland and Meggitt, 1966).

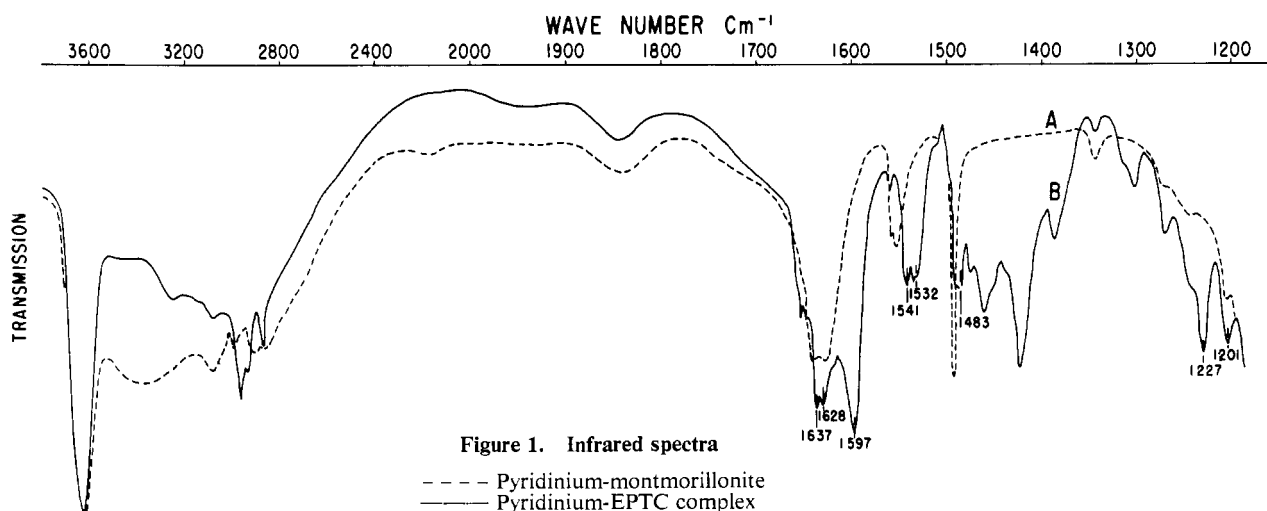
These shifts of the C—O frequency downward and the C—N frequency upward in comparison with the liquid EPTC are indicative of interaction through the carbonyl group which has resulted in a decrease in force constant for the C—O bond and an increase in that of the C—N bond. This interaction can be a hydrogen bonding of the carbonyl oxygen with the pyridinium cation on the exchange complex of the clay. This idea is supported by changes which appear in the spectrum of the pyridinium ion upon complexing with EPTC. Of most significance is the shift of the bands at 1554 and 1561 cm^{-1} to 1532 and 1541 cm^{-1} upon complexation with EPTC. This band involves in-plane N—H bending and would be expected to be affected if hydrogen bonding occurred with a carbonyl group.

The presence of two bands suggests two kinds of pyridinium ion. The author suggests that one (1554 cm^{-1}) is pyridinium cation, directly neutralizing a cation exchange site, while the other (1561 cm^{-1}) is pyridinium cation associated with hydrated aluminum on the exchange complex. The pyridinium-clay suspension was about 2 years old. Fresh pyridinium-montmorillonite gives only the 1554- cm^{-1} band. Upon long standing, undoubtedly some aluminum is released from the lattice, giving rise to the above phenomenon. Since the bands were of about equal intensity, the author presumed that about equal proportions of the two categories of pyridinium were present. Another change in the spectrum of pyridinium-montmorillonite upon complexation with EPTC is the shift of the band at 1494 to 1483 to 1489 cm^{-1} . Farmer and Mortland (1966) observed this band to shift to 1490 cm^{-1} in pyridinium-benzene complexes, and Serratosa (1968) reported it at 1487 cm^{-1} in pyridinium-chlorobenzene-montmorillonite complexes. The bands of the pyridinium ion appearing at 1643 cm^{-1} are shifted downward to 1628 and 1637 cm^{-1} upon interaction with EPTC. The appearance of two bands again suggests two species of pyridinium cation. The presence of considerable water in the air-dry pyridinium-clay film may interfere with the observation of two bands. Complexation with EPTC expels much water, as indicated by the spectra in Figure 1.

The stability of the complex was investigated. When the pyridinium-EPTC-clay complex was heated at 70° C. for 16 hours, all noncomplexed EPTC was expelled and 0.7 mmole of EPTC remained per gram of clay as determined from the absorbance of the 1420- cm^{-1} band. Further heating at 70° C. for 40 hours did not result in any change in spectrum or content of EPTC, suggesting a relatively stable system. The 0.7 mmole of EPTC results in a 1-to-1 ratio of pyridinium and EPTC, suggesting that each

Table I. Observed Frequencies (Cm.⁻¹) for Pyridinium- and Pyridinium-EPTC-Montmorillonite Complexes

Pyridinium-Montmorillonite	Pyridinium-EPTC-Montmorillonite Complex		Liquid EPTC	Assignment
	Pyridinium	EPTC		
683				B ₂ 11
752				B ₂ 4
1206	1201			A ₁ 9a
		1227	1222	C—N
1250				B ₁ 9b
1345				B ₁ 3
1494	1483-1489			A ₁ 19a
1554	1532			B ₁ 19b
1561	1541			
1643	1637	1597	1655	C—O
	1628			A ₁ 8a
2880-3260				N—H
3020-3200		2880-3000		C—H



pyridinium was associated with one EPTC molecule, in accordance with the above idea of hydrogen bonding between pyridinium N—H and the carbonyl of EPTC. Such an interaction would be limited to a 1-to-1 ratio. When these complexes were immersed in distilled water, pyridinium and EPTC disappeared gradually at approximately the same rate, as indicated by the infrared absorption. This disappearance was considerably slower than loss of EPTC from complexes with montmorillonite saturated with metal cations and reported by Mortland and Meggitt (1966). Probably the pyridinium cation gradually hydrolyzes and the pyridine and EPTC move out of the interlamellar region of the mineral.

The measured 001 spacing of pyridinium-montmorillonite is 12.5 Å., while that of the stable pyridinium-EPTC-montmorillonite complex was 13.6 Å. with several integral orders observed. A comparison of infrared spectra of the complex obtained when the clay film was at right angles and at 45° to the incident radiation indicated an increase in absorption intensity of about 20% for the A₁19a species of the pyridinium cation near 1490 cm.⁻¹ and a small undetermined increase in intensity of the A₁8a species near 1640 cm.⁻¹ These bands do not change intensity in pyridinium-montmorillonite where the pyridinium is lying parallel with the clay sheets. Since these bands correspond to vibrations resulting from dipole change along

the C₂ axis, this suggests that the pyridinium cation in the complex is tilted at some angle with respect to the silicate sheets in accord with the 001 spacing of 13.6 Å. This is not the extent observed by Serratos (1968) for pyridinium-chlorobenzene complexes, where he concluded that the pyridinium ion was nearly vertical with respect to the silicate layers. He found greater intensity change for these two bands and a corresponding 001 spacing of 15.0 Å.

Apparently, pyridinium-montmorillonite forms a relatively stable complex with the herbicide EPTC. It seems likely to the author that in soils, organic compounds interacting with clay may facilitate the adsorption and complexation of pesticides on clay minerals, as has occurred in the model system investigated in this work.

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