

INTERACTION OF FLUAZIFOP WITH Al-, Fe³⁺-, AND Cu²⁺-SATURATED MONTMORILLONITE

G. MICERA,¹ A. PUSINO,² C. GESSA,² AND S. PETRETTO²

¹ Dipartimento di Chimica, Università di Sassari
Via Vienna 2, 07100 Sassari, Italy

² Istituto di Chimica Agraria, Università di Sassari
Via E. de Nicola 10, 07100 Sassari, Italy

Abstract—The adsorption of the pesticide Fluzifop, (RS)-2-[4-[[[(5-trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid, on homoionic Cu²⁺-, Fe³⁺-, and Al-bentonites was investigated by infrared and electron spin resonance spectroscopy. For comparison, the binary complexes of the acid containing the above ions were prepared and characterized. On the whole, the results show that the interaction of the acid with the clay may have involved both the protonation of the pyridine nitrogen atom, due to a proton transfer from the acid metal-bound water, and the formation of direct bonds between the carboxylate groups and the exchange cations. The extent of these interactions was dependent on the nature of the metal ions, the Cu ions being more effective in producing CHCl₃-extractable neutral carboxylate complexes, while Al and Fe favored the formation of species bearing protonated nitrogen atoms and undissociated carboxyl groups.

Key Words—Adsorption, Electron spin resonance, Fluzifop, Infrared spectroscopy, Interlayer cations, Pesticide.

INTRODUCTION

Adsorption by clay minerals is one of the most important factors governing the fate and behavior of pesticides in soil (Mortland, 1975), and it may also strongly affect the extent of other processes. The reversibility of pesticide adsorption of clays is of fundamental importance, inasmuch as irreversible adsorption may produce a permanent soil contamination as well as block part of the soil cation-exchange capacity (CEC) (White, 1976).

One aspect of clay-pesticide adsorption that should be considered is the mechanism by which the pesticide is held by the clay minerals. Studies on the adsorption of Fluzifop-butyl, a recently introduced herbicide, by bentonite (Gessa *et al.*, 1987) have shown irreversible adsorption in the cationic form, due to the protonation of the pyridinic nitrogen. Such adsorption drastically reduced the CEC of the clay. Fluzifop-butyl is rapidly hydrolyzed in most aerobic soils, with a half-life of <3 days, to the free acid, Fluzifop (see below) (Bewick, 1986). Other studies (Carr, 1986) have indicated that Fluzifop is the most likely phytotoxic moiety of Fluzifop-butyl. Therefore, the present study was undertaken to learn the mechanism of interaction between Fluzifop and bentonite, a clay of the montmorillonite-type.

EXPERIMENTAL

Materials

The <2- μ m size fraction of bentonite from Ponza, Italy, was obtained by sedimentation. X-ray powder diffraction analysis showed the clay to be predominantly montmorillonite, with traces of illite and quartz. The structural formula, calculated from chemical analyses obtained by dissolution of a sample with HF in a Perkin-Elmer digestion bomb and analysis with a Beckman Spectraspan IV spectrometer, is (Si_{7.856}Al_{0.144})(Al_{3.133}Fe³⁺_{0.254}Mg_{0.593})(OH)₄O₂₀. Its surface area, determined by the ethylene glycol monoethyl ether (EGME) method (Carter *et al.*, 1965), is 643 m²/g. The Fe³⁺-, Al-, and Cu²⁺-exchanged samples were prepared by exposing the clay to 1 N solutions of the corresponding metal chlorides for 24 hr. The samples were then centrifuged and washed with deionized water repeatedly until a test of the supernatant solution for chloride was negative. They were then dried at room temperature.

Fluzifop (C₁₅H₁₂F₃NO₄), structurally (RS)-2-[4-[[[(5-trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid, was prepared by alkaline hydrolysis of Fluzifop-butyl, supplied by ICI Solplant, according to the following procedure: 40 ml of a 1 N NaOH solution was added to 1 g of oily Fluzifop-butyl. The suspension was stirred at room temperature until clear (about 48 hr). After the solution was washed with chloroform, 1 N HCl was added and the acid precipitated. It was filtered and recrystallized from ethanol, giving 0.80 g of product (white crystals, m.p. 101°–102°C). The com-

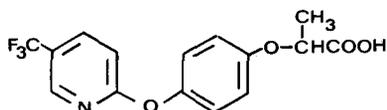


Table 1. Analytical data and proposed stoichiometry for the complexes.¹

Complex	C (%)	H (%)	N (%)	H ₂ O ² (%)
Cu(C ₁₅ H ₁₁ F ₃ NO ₄) ₂ ·2H ₂ O	49.16 (47.91)	3.06 (3.48)	3.84 (3.72)	5.0 (4.79)
Al(C ₁₅ H ₁₁ F ₃ NO ₄) ₂ OH·H ₂ O	50.86 (50.43)	3.58 (3.53)	4.04 (3.92)	2.5 (2.52)
Fe(C ₁₅ H ₁₁ F ₃ NO ₄) ₂ OH·2H ₂ O	47.26 (47.32)	3.50 (3.57)	3.94 (3.68)	5.0 (4.73)

¹ Calculated values in parentheses.² Thermogravimetric determination.

pound was soluble in organic solvents, but only sparingly in water.

Fluazifop hydrochloride was obtained by bubbling HCl into a chloroform solution of Fluazifop. The precipitate was filtered and dried in vacuo.

The Fe³⁺ and Al complexes of Fluazifop were prepared by mixing warm equimolar aqueous solutions of the acid (1.5×10^{-3} mole in about 5 ml, pH 6.2) and Fe(NO₃)₃·9H₂O or AlCl₃·6H₂O (1.5×10^{-3} mole in about 2 ml). On cooling at 0°C, precipitates were obtained, filtered, and washed with ethanol (99.5%, 0°C). Crystals produced by recrystallization from a small amount of boiling water were washed with ethanol. The Cu²⁺ complex was prepared similarly, but precipitation occurred immediately. The product was recrystallized in ethanol (99.5%). Microanalytical (C, H, and N) and thermogravimetric data were consistent with a 1:2 metal : ligand molar ratio for all three complexes. Therefore, the stoichiometry shown in Table 1 is proposed for the complexes.

Adsorption of pesticide

The adsorption of the pesticide onto the clay surfaces was carried out by immersing air-dried, self-supporting clay films into a 20% solution of Fluazifop in CHCl₃. After 24 hr the films were separated from the solution, washed with CHCl₃ to remove excess pesticide, and then air-dried. The amount of copper released into solution after CHCl₃ washing was determined with a Beckman Spectraspan IV spectrometer.

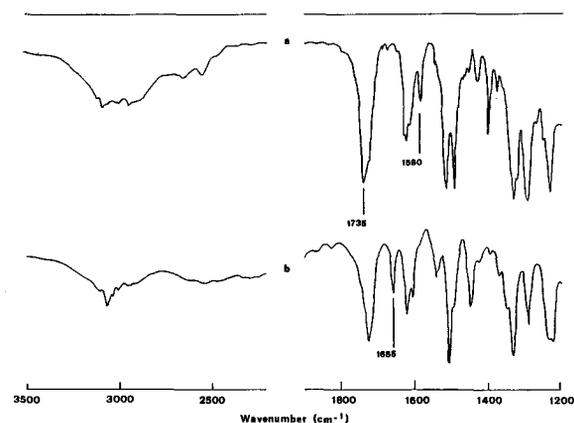


Figure 1. Infrared spectra (KBr disks) of (a) Fluazifop and (b) its hydrochloride.

Physical measurements

Infrared (IR) spectra were recorded with a Perkin-Elmer 683 spectrophotometer. Those for Fluazifop, Fluazifop hydrochloride, and the metal complexes were obtained using KBr disks, whereas those for the pesticide-clay complexes were obtained as differential spectra using self-supporting films. The IR spectrum of Fluazifop was recorded also in a CHCl₃ solution. Electron spin resonance (ESR) measurements at X-band were carried out at room temperature using a Varian E 9 spectrometer. Microanalyses (C, H, and N) were made using a Perkin-Elmer 240 analyzer. Thermogravimetric measurements were made on a Perkin-Elmer TGS 2 apparatus at the heating rate of 5°C/min under a nitrogen flow.

RESULTS AND DISCUSSION

The IR spectra of Fluazifop and Fluazifop-hydrochloride are compared in Figure 1. The main distin-

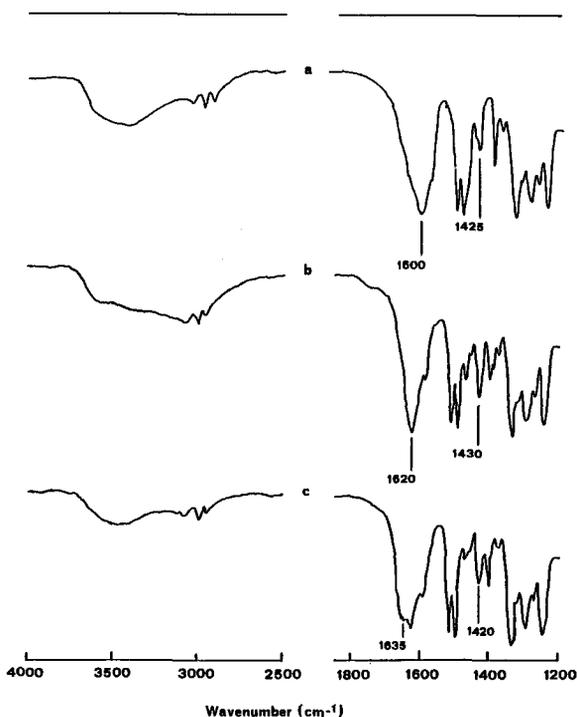


Figure 2. Infrared spectra (KBr disks) of (a) Al, (b) Fe, and (c) Cu complexes of Fluazifop.

Table 2. Infrared absorptions (cm^{-1}) of carboxylate groups for metal and metal-clay complexes of Fluzifop.¹

Metal complexes			Metal-clay complexes		
Metal	ν_{as}	ν_{s}	Metal	ν_{as}	ν_{s}
Al	1600s	1450m	Al	1600sh	2
Fe	1620s	1430m	Fe	1620s	1430w
Cu	1635sb	1420m	Cu	1590s	2

¹ ν_{as} and ν_{s} = carboxylate antisymmetric and symmetric stretches, respectively.

² Not detected.

s = strong, m = medium, w = weak, sh = shoulder, b = broad.

guishing features of protonated Fluzifop are: (1) the occurrence of a weak absorption in the N–H stretching region centered at 3065 cm^{-1} due to the protonated pyridinic nitrogen, and (2) the shift of the ν_{sa} ring vibration from 1580 cm^{-1} (Wilmshurt and Bernstein, 1957) to 1655 cm^{-1} , the latter value being typical of pyridinium compounds (Cook, 1961; Farmer and Mortland, 1966).

The 1735-cm^{-1} absorption of the free carboxyl group is absent, and two bands in the ranges $1600\text{--}1635$ and $1420\text{--}1430\text{ cm}^{-1}$, attributable to the $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ modes, respectively, of a metal-bound carboxylate group, are present in the spectra of the Fe^{3+} , Al, and Cu^{2+} complexes of Fluzifop (Figure 2 and Table 2).

The band assignments made for Fluzifop and its complexes were used to interpret the spectra of the clay-Fluzifop complexes. The IR spectra of Fe^{3+} , Al, and Cu^{2+} -clay-Fluzifop complexes (Figure 3) were significantly different from each other and from the spectrum of the acid in KBr. In all spectra (1) a weak and broad absorption in the $3090\text{--}3115\text{-cm}^{-1}$ range (N–H stretch) and a band at 1655 cm^{-1} (ν_{sa}) exist, both indicative of pyridinium ions; (2) bands are present in the $1590\text{--}1620\text{-cm}^{-1}$ range, assigned to $\nu_{\text{as}}(\text{COO})$; and (3) a band at $1740\text{--}1750\text{ cm}^{-1}$ assigned to the stretching mode of the un-ionized carboxyl group was observed. Deuteriation shifted the NH-stretching bands toward lower wavenumbers ($\nu_{\text{H}}/\nu_{\text{D}} \approx 1.06$). The $\nu_{\text{sym}}(\text{COO})$ mode was easily distinguishable for the Fe complexes (1430 cm^{-1}), but the assignment was more difficult for Cu and Al complexes.

It should be noted that the IR spectra of the acid showed a stretch absorption at 1735 and 1740 cm^{-1} in KBr and CHCl_3 , respectively, indicating that the un-ionized carboxyl groups of the adsorbed molecules scarcely interacted with the surroundings, and, if the spectral differences are significant, they were less perturbed by hydrogen bonds than in the pure state or in CHCl_3 solution.

Despite these common features, remarkable differences were observed in the spectra of the three complexes. The intensities of the NH and COOH absorp-

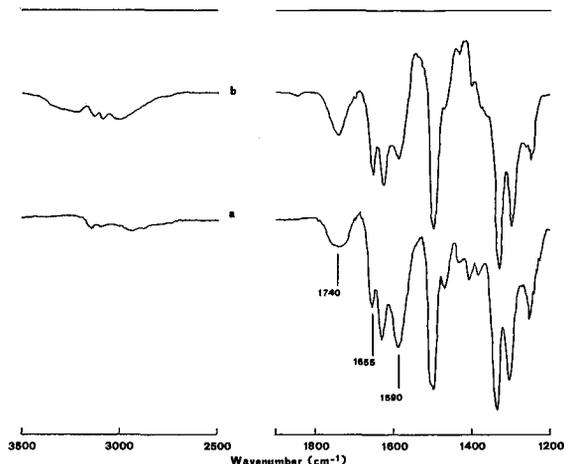


Figure 3. Infrared differential spectra of Fluzifop-treated homoionic clays: (a) Cu and (b) Cu after CHCl_3 washing.

tions were, in fact, higher for the Al and Fe complexes, whereas an opposite trend was observed for the carboxylate bands. These observations suggest that the adsorbed molecules may have contained both pyridinic and carboxyl groups in protonated or deprotonated forms, the extent of protonation being higher in the Fe and Al clays.

After the adsorption of Fluzifop, part of Cu, contrary to Al and Fe, was apparently extracted by repeatedly washing with chloroform and, after removal of the solvent, was recovered as the corresponding binary complex with Fluzifop (see below). Typically, almost 10% of Cu was extracted from the clay treated with an amount of pesticide equivalent to its CEC, whereas much less Cu was extracted for lower Fluzifop concentrations. After Cu extraction, the intensity of the carboxylate bands in the IR spectra was less than before washing (Figure 3). This behavior is different from that previously observed by Gessa *et al.* (1987) for the butyl ester of Fluzifop. No significant amount of metal ions was released from clays treated with the ester, indicating that the interaction involved only pesticide molecules protonated at the nitrogen atom and electrostatically bound to the clay interlayer. Evidently, adsorption of Fluzifop on clay produced CHCl_3 -extractable neutral species, in addition to the organic cations.

The Cu^{2+} -clay complexes formed by Fluzifop and its butyl ester were studied by ESR spectroscopy. Although slight, the spectral differences were enough to allow reasonable hypotheses about the chemical form of Cu in the interlayer. In fact, the spectra of the Cu-clays, untreated and treated with Fluzifop butyl ester, were similar to each other and consisted of isotropic resonances due to the freely tumbling hexa-aquaion for the hydrated samples and anisotropic signals ($g_{\parallel} = 2.35$, $A_{\parallel} = 165 \times 10^{-4}\text{ cm}^{-1}$), most likely due to the tetra-

aquaion in the interlayer for the samples heated at 120°C (Figures 4a and 4b). In contrast, those of the samples treated with Fluazifop showed anisotropic signals ($g_{\parallel} = 2.31$ and $A_{\parallel} = 170 \times 10^{-4} \text{ cm}^{-1}$) (Figure 4c), suggesting that Cu^{2+} was immobilized in mononuclear arrangements, having a coordination geometry more elongated than that in the untreated Cu-clays. These changes may be expected, e.g., upon substituting at least part of the equatorially bound water of the aquaion by carboxylate groups.

Reliable structural information was obtained only for the Cu^{2+} complex of Fluazifop. The powder ESR spectra is typical of dinuclear copper(II) complexes in the triplet state ($g_{\parallel} = 2.34$, $g_{\perp} = 2.08$, and zero-field splitting $D = 0.34 \text{ cm}^{-1}$) clearly indicating a dimeric, tetra-carboxylate-bridged arrangement for the Cu^{2+} ions (therefore different from those formed in the clay), like that occurring in cupric acetate monohydrate (Brown and Chidambaram, 1973). Accordingly, the IR absorptions of the carboxylate groups were significantly different from those in the clay-Fluazifop complexes. Based on the coincidence of the carboxylate absorptions, the Al (and Fe) structures in the complexes and in the Fluazifop-treated clays may be the same.

CONCLUSIONS

The results of this study clearly demonstrate that the adsorption of Fluazifop in the interlayer of smectite clays occurs by means of more than one interaction mechanism. The first mechanism involves the protonation of the pyridinic nitrogen atom by the acid water associated with the exchangeable cations, analogous to the behavior of Fluazifop-butyl. Another adsorption mechanism, which is peculiar for Fluazifop, is connected with the coordination of carboxylate groups to the exchange metal ions.

These mechanisms could be related; in fact, the formation of a pyridinium ion should consume surface protons and decrease the surface acidity, thereby, promoting the dissociation of the COOH groups.

Thus, several species should arise from such interactions: (1) Fluazifop molecules containing protonated pyridinic and un-dissociated carboxyl groups; (2) Fluazifop molecules containing protonated pyridine nitrogens, but deprotonated carboxylic groups bound to the metal ions, and (3) adsorbed molecules having deprotonated nitrogens and metal-bound carboxylates. The distribution of these species should vary mainly as a function of the interlayer water acidity, which is metal-ion dependent. Among the ions herein considered, Cu^{2+} is well-known to be responsible for acidic properties weaker than those of Fe^{3+} and Al ions. Thus, the species distribution in the Cu^{2+} -clay-complexes should be more shifted toward species (2) and (3).

This conclusion is supported not only by the IR results, which indicate that the protonated groups are

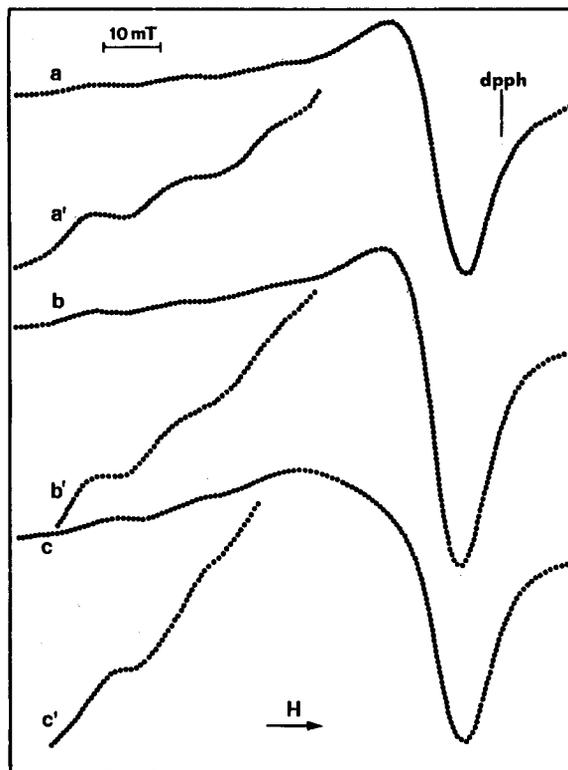


Figure 4. X-band electron spin resonance spectra of (a) Cu-bentonite after heating at 120°C, (b) Cu-bentonite treated with Fluazifop-butyl after heating at 120°C, and (c) Cu-bentonite treated with Fluazifop. Expanded spectra of a, b, and c are labelled by a', b', and c', respectively.

less numerous in the Cu^{2+} clays, but also by the fact that part of Cu may have been extracted and thus should be present in the interlayer mostly in the form of neutral (3) species.

Presumably, other factors, such as the complexity of the molecular structure, could contribute to make Cu more extractable than Al and Fe. In fact, the Cu-clay-Fluazifop complex should adopt a rather simple structure, in which, as suggested by the spectral results, the Cu^{2+} ion is bound to two monodentate carboxylate groups and two water molecules. In contrast, the interlayer Fe^{3+} and Al complexes, as is usual in the coordination chemistry of these ions, may form more complicated structures, possibly charged and/or polynuclear.

ACKNOWLEDGMENTS

This research was supported in part by M.P.I.

REFERENCES

- Bewick, D. W. (1986) Stereochemistry of Fluazifop-butyl transformations in soil: *Pest. Sci.* 17, 349–356.
Brown, G. M. and Chidambaram, R. (1973) Dinuclear cop-

- per(II) acetate monohydrate: A redetermination by neutron-diffraction analysis: *Acta Cryst.* **B29**, 2393–2403.
- Carr, J. E. (1986) The uptake, translocation and metabolism of Fluazifop-butyl: *Pestic. Sci.* **17**, 58–64.
- Carter, D. L., Heilman, M. D., and Gonzales, C. S. (1965) Ethylene glycol monoethyl ether for determining surface area of silicate minerals: *Soil Sci.* **100**, 356–360.
- Cook, D. (1961) Vibrational spectra of pyridinium salts: *Can. J. Chem.* **39**, 2004–2024.
- Farmer, V. C. and Mortland, M. M. (1966) An infrared study of the coordination of pyridine and water to exchangeable cations in montmorillonite and saponite: *J. Chem. Soc. A*, 344–351.
- Gessa, C., Pusino, A., Solinas, V., and Petretto, S. (1987) Interaction of Fluazifop-butyl with homoionic clays: *Soil Sci.*, **144** (in press).
- Mortland, M. M. (1975) Interactions between clays and organic pollutants: in *Proc. Inter. Clay Conf., Mexico City, 1975*, S. W. Bailey, ed., Applied Publishing, Wilmette, Illinois, 469–475.
- White, J. L. (1976) Clay-pesticide interactions: in *Bound and Conjugated Pesticide Residues*, D. D. Kaufman, G. G. Still, G. D. Paulson, and S. K. Bandal, eds., *ACS Symp. Ser. No. 29*, Amer. Chem. Soc., Washington, D.C., 208–218.
- Wilmschurt, J. K. and Bernstein, H. J. (1957) The vibrational spectra of pyridine, pyridine-4-d, pyridine-2,6-d₂ and pyridine-3,5-d₂: *Can. J. Chem.* **35**, 1183–1194.

(Received 28 May 1987; accepted 22 January 1988; Ms. 1676)