Clays and Clay Minerals, 1972, Vol. 20, pp. 359–367. Pergamon Press. Printed in Great Britain

REACTIONS BETWEEN FULVIC ACID AND Cu^{2+}-MONTMORILLONITE*

M. SCHNITZER and H. KODAMA
Soil Research Institute, Canada Department of Agriculture, Ottawa, Ontario, Canada

(*Received* 16 *April* 1972)

Abstract—Shaking of water-soluble fulvic acid with Cu^{2+}-montmorillonite at pH 2·5 increased the interlamellar spacing from 10·0 to 15·1 Å. The spacings were measured at ≈ 0% relative humidity. The extent of interlayer adsorption decreased with increase in pH. Differential thermal analysis and thermogravimetric examinations showed that in addition to interlayer adsorption, fulvic acid was also retained on external clay surfaces. The FA was held so tightly by the Cu^{2+}-clay that > 3/4 of the total amount adsorbed, including degradation products formed from it, resisted decomposition even when heated to 1000°C. I.R. spectra showed that β-diketone groups in fulvic acid reacted with Cu^{2+} in or on the clay to form acetylacetonate-type chelates. Indications were obtained that the mechanism postulated for the FA–Cu^{2+}-clay interaction may also apply to reactions between FA and montmorillonite saturated with other di- and trivalent metal ions. Reactions of FA in aqueous solutions with metal ions in the presence of clays differ from those in the absence of clay. Montmorillonite appears to affect the conformation of the fulvic acid polymer in a way that favours reactions between C=O groups and metal ions, a type of reaction that has so far not been observed in aqueous solutions in the absence of clay.

INTRODUCTION

In soils and sediments humic substances interact with clays to form complexes of widely differing stabilities and properties. It has been estimated that between 52 and 98 per cent of the organic carbon in soils occurs in the form of clay—organic complexes (Greenland, 1965), so that a more adequate knowledge of the synthesis, stability and characteristics of these complexes would assist pedologists and geochemists in better understanding the physical, chemical and biological properties of soils and waters. Although the literature contains a considerable amount of information on reactions of clays with known organic compounds of relatively simple molecular structures (Greenland, 1971; Mortland, 1970), little is known about reactions of clays with naturally occurring high-molecular weight organic substances extracted from soils and sediments.

In previous investigations, the authors reported on reactions of fulvic acid (FA), a water-soluble humic material widely occurring in soils and waters, with montmorillonite. FA was found to react with the clay by adsorbing on its outer surfaces and in interlamellar spaces. The latter type of adsorption depended on the pH of the reaction medium (Schnitzer and Kodama, 1966), the FA concentration (Schnitzer and Kodama, 1967), the time of reaction and the type of interlayer cation with which the clay was saturated (Kodama and Schnitzer, 1968; Schnitzer and Kodama, 1969). It was estimated by differential thermal analysis (DTA) and by differential thermogravimetric analysis (DTG) that about 50% of the FA was adsorbed by the clay in its interlayer spaces, with the remainder on external surfaces (Kodama and Schnitzer, 1969). More recently, we (Kodama and Schnitzer, 1971) were able to demonstrate the occurrence, in nature, of interlayer-adsorbed FA by isolating a FA–clay complex from the Ae horizon of a Humo–Ferric Podzol soil.

In view of the practical significance of the problem, we felt that additional work on reactions of FA with montmorillonite, using chemical, X-ray, IR, ESR and thermal methods was warranted. Since i.r. spectra of FA–Cu^{2+}-montmorillonite and of FA–Al^{3+}-montmorillonite complexes showed hitherto undetected bands near 1525 cm^{-1}, we concentrated our efforts on examining, in greater depth, interactions between FA and Cu^{2+}-montmorillonite with the overall objective of gaining a better understanding of the mechanism(s) involved in reactions between FA and clays.

MATERIALS AND METHODS

FA

The FA originated from the Bh horizon of the Armadale soil, an imperfectly drained Podzol developed on sandy loam in Prince Edward

---

*Contribution No. 419.

Island, Canada. Methods of extraction and purification of the FA were analogous to those described previously (Schnitzer and Skinner, 1963). The extracted and purified FA contained 1·0% ash; its elementary composition on a dry, ash-free basis was: C, 50·90; H, 3·35; N, 0·75; S, 0·25; O, 44·75%. One g. of FA contained 9·1 meq. CO_2H, 3·3 meq. phenolic OH, 3·6 meq. alcoholic OH, 2·6 meq. ketonic C=O and 0·6 meq. quinone groups (Schnitzer and Riffaldi, 1972). Its number-average molecular weight ($\bar{M}n$), measured by vapor pressure osmometry, and corrected for dissociation of CO_2H groups, was 945 (Hansen and Schnitzer, 1970). From the molecular weight, ultimate and functional group analyses the following molecular formula was calculated: $C_{28}H_{16}(CO_2H)_9(OH)_7(CO)_3$.

Montmorillonite

The montmorillonite used was the 0·2–2·0 μ fraction of a Wyoming bentonite, separated by a combination of sedimentation and centrifugation procedures. Separate clay suspensions were saturated with concentrated chloride or sulfate solutions of Ag^{1+}, Au^{1+}, NH_4^{1+}, Cu^{2+}, Co^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sn^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+} and Fe^{3+}. Each clay system was then dialyzed against distilled water until free of anions and freeze-dried.

Preparation of FA montmorillonite complexes

One hundred mg of FA was weighed into a 35-ml graduated ground glass-stoppered centrifuge tube and dissolved in 15 ml of distilled water. To the resulting solution 40 mg of clay was added, the pH adjusted to the desired level with 0·2 N NaOH solution and the volume made up to 20 ml with distilled water. It is possible that some of the Na^+ added modified the cation population on the clays. The tube and content was agitated on a reciprocating shaker at room temperature for 36 h, then centrifuged at 2,000 rpm for one hour. The supernatant solution was decanted. The residue was shaken for one hour with 20 ml of distilled water adjusted to the desired pH; the supernatant solution was separated by centrifugation for one hour at 2,000 rpm. The residue was dried in a vacuum desiccator over P_2O_5 at room temperature, while the supernatant solution plus washings were dried on the steambath and analyzed for *C* by dry-combustion with V_2O_5 as a catalyst (Schnitzer and Kodama, 1967).

Differential thermal analysis (DTA)

DTA curves were recorded on a Robert L. Stone DTA apparatus. Usually 10 mg of sample, diluted with 10 mg of alumina, was sandwiched between layers of alumina and heated under static air.

Thermogravimetric analysis (TGA)

Thermogravimetric analyses were done on a Fisher Balance Assembly mounted over a cylindrical furnace enclosing a suspended platinum dish. The heating rate was 5°C per min.

X-ray analysis

Basal spacings (d_{001}) were measured on oriented aggregates on glass slides using a Philips diffractometer. Experimental conditions were as follows: Fe-filtered Co-radiation (Co $K\alpha$; $\lambda = 1{\cdot}7902$ Å), 50 Kv, 10 mA, scanning speed 0·5° (2θ)/min. All measurements were made under extremely dry conditions ($\approx$ 0% relative humidity).

I.R. spectra

Samples were prepared by evaporating at room temperature and pressure on Al-foil aqueous suspensions of clays and FA–clay complexes. The resulting thin, self supporting films were then peeled away from the Al-foil surface and mounted in a holder. In the case of FA, a concentrated solution was pipetted onto a CaF_2 disc and allowed to dry at room temperature.

Pleochroic effects were estimated by observing differences in absorption intensities with the film positioned at 20, 40 and 55° to the path of the i.r. spectrophotmetric beam. Spectra were recorded on a Beckman i.r. 12 spectrophotometer.

E.S.R. spectra

ESR spectra were recorded on powders at room temperature on a Varian E-3 spectrometer.

Analytical methods

For the determination of Cu^{2+} in the supernatant solutions and washings, portions were dried on the steambath, digested with 1 : 1 HNO_3–$HClO_4$ solution and then taken up in dilute HCl solution. Cu^{2+} was determined by atomic absorption spectrophotometry. All measurements were corrected for Cu^{2+} in reagents and distilled water.

RESULTS AND DISCUSSION

Reaction of FA with Cu^{2+}–montmorillonite

The d_{001} of the initial Cu^{2+}–montmorillonite was 10·0 Å; after interaction with FA the spacing increased to a maximum of 15·1 Å at pH 2·5 (Table 1). Interplanar spacings were pH-dependent and decreased with increase in pH, with the steepest decrease occurring between pH 3·5 and 4·5, which is the region into which the overall apparent pK of the FA falls (Schnitzer and Kodama, 1966). This suggested that the magnitude of the d_{001}

Table 1. Adsorption of Fulvic acid (FA) by 40 mg of Cu^{2+}-montmorillonite at various pH levels

pH	mg FA adsorbed	d_{001} (Å)
2·5	26·8	15·1
3·5	17·4	13·7
4·5	15·8	10·9
5·5	13·9	10·4
6·5	12·8	10·2

spacing was related to the degree of ionization of the functional groups, particularly the CO_2H groups, in the FA. The reaction of FA with Cu^{2+}–montmorillonite resembled that previously reported for FA and Na-montmorillonite (Schnitzer and Kodama, 1966). Amounts of FA adsorbed by the clay followed d_{001} values (Table 1), thus demonstrating that FA was responsible for increases in d_{001} spacings.

Since FA is known to form relatively stable water-soluble complexes with Cu^{2+} (Schnitzer and Hansen, 1970; Gamble *et al.*, 1970), it appeared possible that complex formation was involved in the interaction of FA with Cu^{2+}–montmorillonite. To test this point, amounts of Cu^{2+} were determined in supernatant solutions and washings from clays that had interacted with FA and with distilled water at pH levels ranging from 2·5 to 6·5. As shown in Table 2, amounts of Cu^{2+} brought into solution by 100 mg of FA ranged from 650·3 to 848·7 μg, while distilled water solubilized between 412·0 μg (at pH 2·5) and 90·0 μg of Cu^{2+} (at pH 6·5). The fourth column in Table 2 lists differences (Δ) between Cu^{2+} solubilized by FA and by distilled water. These ranged from 238·3 μg to 758·7 μg, and were most likely the lowest amounts of Cu^{2+} that had been complexed by the FA. Since 40 mg of Cu^{2+}–montmorillonite contained 1080·0 μg of Cu^{2+}, the amounts of Cu^{2+} solubilized and complexed by the FA ranged from 60 to 79% of the total Cu^{2+} in the clay. It can be calculated from the data in Tables 1 and 2 that the supernatant solutions of the FA–clay systems at the different pH levels contained between 77·5 (at pH 2·5) and 93·2 (at pH 6·5) μ moles of FA, which provided, in terms of mole concentrations, for an excess of FA over Cu^{2+} in solution ranging from 7·6 (at pH 2·5) to 6·9 (at pH 6·5).

Table 2. Amounts of Cu^{2+} solubilized by 100 mg of FA and by distilled water from 40 mg of Cu^{2+}-montmorillonite

	μg Cu^{2+} solubilized by		
pH	FA	distilled water	Δ
2·5	650·3	412·0	238·3
3·5	797·1	298·0	499·1
4·5	818·0	250·0	568·0
5·5	850·7	212·0	628·7
6·5	848·7	90·0	758·7

The magnitude of pH-drop on addition of metal ions to aqueous solutions of organic ligands is often taken as an indication of complex formation (Martell and Calvin, 1952). To further check on possible complex formation between FA and Cu^{2+} in and on the clay, we added to 100 mg of FA dissolved in 18 ml of distilled water and carefully adjusted to pH 3·50, 40 mg of Cu^{2+}–montmorillonite. Following thorough mixing of the reactants, the pH dropped to 3·40, and it required 0·12 ml of 0·1 N NaOH solution to readjust the pH to 3·50. Periodic checks of the pH after 4, 6, 12 and 24 h found it to remain constant at 3·50. The amount of base that was required to readjust the pH to 3·50 was equivalent to the neutralization of 0·012 meq of protons that were apparently released by the FA when it complexed 380 μg of Cu^{2+}. Thus, approximately 76% of the Δ value (pH 3·5) listed in Table 2 could be accounted for by the pH-drop.

ESR spectra were run on: (a) Cu^{2+}–montmorillonite; (b) a FA–Cu^{2+}–montmorillonite complex, prepared at pH 3·5; and (c) on a Cu^{2+}–FA complex, prepared at pH 3·5; the complex was made by dissolving 95·0 mg of FA in 25 ml of distilled water, adding to it 25 ml of an aqueous solution containing 91·1 mg of $CuCl_2.2H_2O$, adjusting the pH to 3·5 and removing the excess Cu^{2+} by dialysis. The molar FA/Cu^2 ratio of the complex was 2·0. E.S.R. spectra of all materials were single asymmetric lines without fine splitting. The e.s.r. spectra for the Cu^{2+}–clay and for the FA–Cu^{2+}–clay complex were very similar to each other and had line widths of 125 G and g-values of about 2·03. The e.s.r. spectrum of the Cu^{2+}–FA complex had a line width of 275 G and a g-value of 2·08. It appeared from the e.s.r. spectra that no appreciable amounts of Cu^{1+} or organic cation radicals were formed during the FA–Cu^{2+}–clay interaction.

The DTA curves of the FA–Cu^{2+}–montmorillonite complex (Fig. 1) showed an endotherm near 100°C, due to dehydration. Exotherms occurred near 340, 440, 640, 700 and 940°C. The exotherms near 640 and 700°C were indicative of the presence of interlayer-adsorbed FA (Kodama and Schnitzer, 1969) and appeared in a temperature region that is similar to that in which exotherms of clay-protein and other clay-organic complexes appear (Bradley and Grim, 1948; Allaway, 1949; Talibudeen, 1952). The endotherm at 840°C and the exotherm at 935°C, which constituted a *S*-shaped curve, are indicative of the reorganiza-

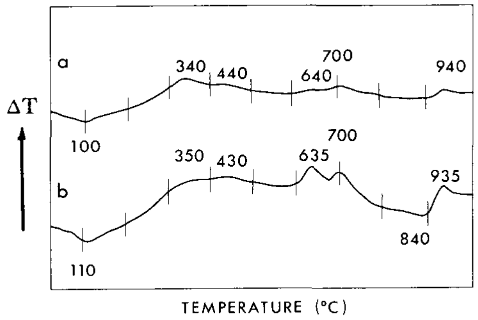


Fig. 1. Differential thermal analysis curve of a FA-Cu^{2+}-montmorillonite complex prepared at pH 3·5; (a) 10 mg sample; (b) 49 mg sample.

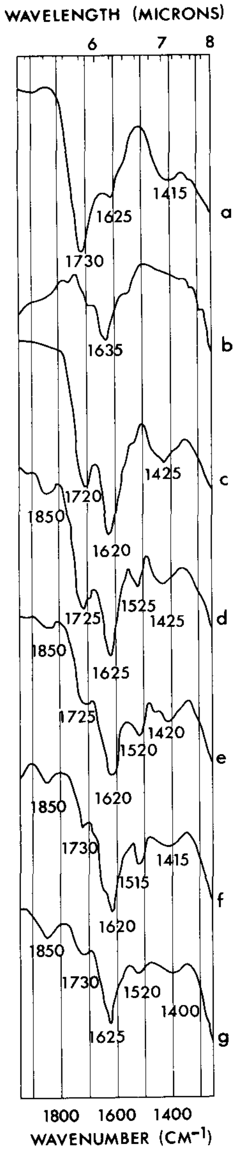


Fig. 2. I.R. spectra of: (a) untreated FA; (b) Cu^{2+}-montmorillonite; (c) FA-Cu^{2+}-montmorillonite complex prepared at pH 2·5; (d) FA-Cu^{2+}-montmorillonite complex prepared at pH 3·5; (e) FA-Cu^{2+}-montmorillonite complex prepared at pH 4·5; (f) FA-Cu^{2+}-montmorillonite complex prepared at pH 5·5; (g) FA-Cu^{2+}-montmorillonite complex prepared at pH6·5.

tion of the clay, which in this instance was accompanied by combustion of FA residues that had persisted up to this high temperature. Judging from the thermal decomposition of FA complexed by Na-montmorillonite (Kodama and Schnitzer, 1969), we believe that the exothermic peaks at 340 and 440°C arose from the combustion of some of the FA adsorbed on the outer surfaces of the clay.

Thermogravimetric analysis of the FA-Cu^{2+}-clay complex was undertaken to quantitatively determine weight losses associated with the major decomposition reactions. Fifty mg of complex prepared at pH 3·5, which contained 20·0 mg of FA and 30·0 mg of clay, lost 2·04 mg of FA between 350 and 550°C and 2·88 mg of FA between 550 and 800°C. The weight loss in the latter temperature range also included H_2O resulting from the dehydroxylation of the clay. Thus, less than about 1/4 of the total FA could be recovered from the complex by heating; the remaining 3/4 was retained so tightly by the Cu^{2+}-clay that it or its oxidation products resisted decomposition even when heated up to 1000°C. If we assume by analogy with the adsorption of FA by Na-montmorillonite (Kodama and Schnitzer, 1969) that about 1/2 of the total FA was adsorbed in interlayer spaces, then the Cu^{2+}-clay prepared at pH 3·5 contained in its interlamellar spaces 10·0 mg ($1{\cdot}1 \times 10^{-5}$ moles) of FA and 0·23 mg ($3{\cdot}6 \times 10^{-6}$ moles) of Cu^{2+}, yielding a molar FA/Cu^{2+} ratio of 3·0. This was equivalent to about eight ketonic C=O and twenty-seven CO_2H groups per atom of Cu^{2+} and thus provided for a large excess of these groups.

I.R. spectra

The i.r. spectrum of untreated FA (Fig. 2, curve a) showed the following major bands in the 1,900–1,400 cm^{-1} region, the most informative ones for assessing metal-FA interactions: 1730 (C=O of CO_2H, C=O stretch of ketonic C=O), 1625 (aromatic C=C, H-bonded C=O of carbonyl, double bond conjugated with C=O, COO^-) and 1415 cm^{-1} (COO^-).

The Cu^{2+}-montmorillonite spectrum (Fig. 2, curve b) showed a strong band near 1635 cm^{-1}, due to adsorbed water. The i.r. spectrum of the

FA–Cu^{2+}-montmorillonite complex prepared at pH 2·5 (Fig. 2, curve c) showed bands at 1720, 1620 and 1425 cm^{-1}, whereas spectra of FA–clay complexes prepared at pH > 2·5 exhibited additional bands at 1850 and near 1520 cm^{-1} (Fig. 2, curves d to g).

The i.r. data are summarized in Table 3, which also shows the relative optical density for each band, with optical densities near 1720 cm^{-1} taken to be equal to 100. The spectra show increases in absorption near 1630 cm^{-1} with increase in pH, indicating increased formation of COO$^-$ groups. It is unlikely that under our experimental conditions humidity contributed much to enhanced absorption in this region. Of special interest were the bands at 1850 and 1520 cm^{-1} in the i.r. spectra of the FA–clay complexes; these bands tended to increase in intensity with increase in pH and were absent in the spectra of the untreated FA and of the clay. A search of the literature indicated that Cu^{2+}–, Pd^{2+}–, and Al^{3+}–acethylacetonates absorb between 1525 and 1535 cm^{-1} and that the absorption arises from the $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ stretching, referred to as the ν_1 band (Nakamoto, 1963). A β-diketone structure, of which the acetylacetone anion (R_1=R_3=CH_3, R_2=H_2) is the simplest representative, is shown in Fig. 3. The chelate ring is planar and symmetrical and the two $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ bonds are equivalent as are the two $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ bonds in the ring (Nakamoto, 1963), which provides strong possibilities for the existence of resonance in the chelate ring. Evidence for the occurrence of β-diketone structures in FA and for their likely participation in reactions with metals was recently provided by the isolation by Ortiz de Serra and Schnitzer (1972) of two complex aromatic anhydrides with β-diketone groups as substituents on the aromatic ring (Fig. 4). These compounds were isolated from products resulting from the permanganate oxidation of methylated FA.

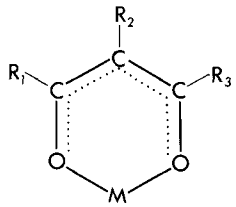


Fig. 3. β-diketone metal chelate.

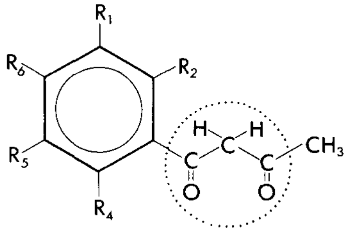


Fig. 4. Compounds produced by the permanganate oxidation of methylated FA. Compound I: $R_1 = CH_2CO_2CH_3$, $R_2 = OCO_2CH_3$, $R_4 = OCO_2CH_3$, $R_5 + R_6 = CO.O.CO$. Compound II: $R_1 = OCO_2CH_3$, $R_2 = COCO_2CH_3$, $R_4 = OCO_2CH_3$, $R_5 + R_6 = CO.O.CO$.

To obtain additional information on the role of C=O groups in the FA–clay interactions, we blocked these groups by forming oximes and semicarbazones by methods described previously (Schnitzer and Skinner, 1965), and then interacted the derivatives with the clay. I.R. spectra of the oximated FA–clay complex (Fig. 5, curve b) and of the FA–semicarbazone-clay complex (Fig, 5, curve c), both prepared at pH 3·5, showed diminution or disappearance of bands at 1850 and 1520 cm^{-1}, indicating that the blocking of C=O groups had prevented these groups from reacting with Cu^{2+}.

Little pleochrism was observed for the major

Table 3. Major bands in i.r. spectra of FA and FA–Cu^{2+}–montmorillonite complexes

Type of material	prepared at pH	cm^{-1}	RI*	cm^{-1}	RI	cm^{-1}	RI	cm^{-1}	RI	cm^{-1}	RI
FA	3·5			1730	100	1625	40			1415	30
FA–clay complex	2·5			1720	100	1620	170			1425	49
	3·5	1850	25	1725	100	1625	145	1525	35	1425	46
	4·5	1850	23	1725	100	1620	256	1520	100	1420	90
	5·5	1855	42	1730	100	1620	323	1515	94	1415	90
	6·5	1850	83	1720	100	1625	333	1520	110	1400	77
tilt = 0°	4·5	1850	23	1725	100	1620	256	1520	100	1420	90
= 20°	4·5	1850	25	1720	100	1620	313	1520	122	1420	97
= 40°	4·5	1850	32	1725	100	1620	263	1520	103	1420	79
= 55°	4·5	1835	19	1730	100	1625	278	1520	111	1420	92

*Relative Intensity

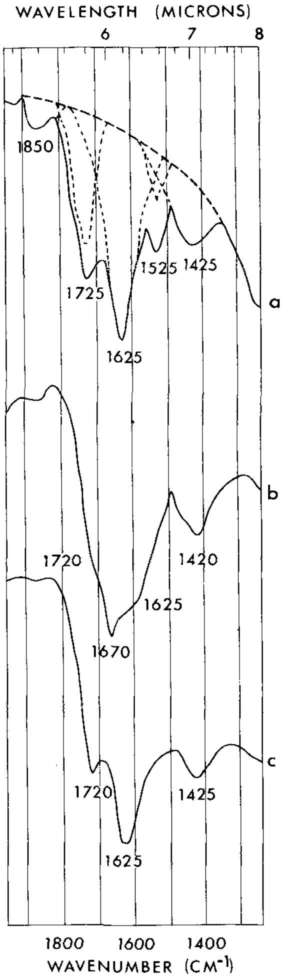


Fig. 5. I.R. spectra of: (a) FA-Cu^{2+}-montmorillonite complex prepared at pH 3·5; (b) FA-oxime-Cu^{2+}-montmorillonite complex prepared at pH 3·5; (c) FA-semicarbazone-Cu^{2+}-montmorillonite complex prepared at pH 3·5.

i.r. bands of a FA–clay complex prepared at pH 4·5 (Table 3).

Reactions between FA and montmorillonite saturated with different cations

To uncover whether montmorillonite saturated with different mono-, di-, and tri-valent metal ions would react with FA by a mechanism that was similar to that of the Cu^{2+}-clay–FA reaction, we interacted different clays with FA, determined the amounts of FA adsorbed and recorded i.r. spectra of the complexes.

In terms of mg of FA adsorbed at pH 3·5, the clays saturated with the different cations followed the order: $Sn^{2+} > Pb^{2+} > Au^{1+} > Al^{3+} > Fe^{3+} = Cd^{2+} > Ag^{1+} > Ni^{2+} > Mn^{2+} > Mg^{2+} > NH_4^{1+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Cr^{3+}$ (Table 4). Thus, the order of adsorption did not follow the valence or the ionization potential of the metal ion nor the magnitude of stability constants of metal-FA complexes (Schnitzer and Hansen, 1970).

Table 4. Amounts of FA adsorbed at pH 3·5 by 40 mg of clay saturated with different cations

Saturating cation	mg FA adsorbed
Ag^{1+}	18·6
Au^{1+}	20·9
NH_4^{1+}	17·7
Cd^{2+}	19·5
Co^{2+}	14·6
Cu^{2+}	17·4
Mg^{2+}	17·8
Mn^{2+}	18·0
Ni^{2+}	18·5
Pb^{2+}	21·0
Sn^{2+}	21·7
Zn^{2+}	16·3
Al^{3+}	19·8
Cr^{3+}	14·3
Fe^{3+}	19·5

I.R. spectra of the different FA–clay complexes exhibited bands at 1850, 1725, 1625, 1460 and 1430 cm^{-1} (Table 5). Only the FA–Cu^{2+} and -Al^{3+}-clay complexes showed bands near 1525 cm^{-1}, whereas the FA–Cu^{2+}-, -NH_4^{1+}- and -Al^{3+}-clay complexes failed to show appreciable absorption near 1460 cm^{-1}, which could have arisen from a combination of ν(C–O) and δ(C–H) vibrations. The absence of bands at 1460 cm^{-1} in the spectra of the FA–NH_4^{1+}-, and FA–Al^{3+}-clay complexes may have been due to masking effects of NH_4^{1+}-deformations near 1430 cm^{-1}; the Al^{3+} clay may have contained NH_4^{1+} as contaminant. It is possible that the ν(C–O) stretching band that occurred near 1525 cm^{-1} in the i.r. spectra of the FA–Cu^{2+}- and FA–Al^{3+}-clay complexes had shifted downwards to near 1460 cm^{-1} in the spectra in the other FA–clay complexes. From the data summarized in Table 5 it appears that the reaction mechanism postulated for the FA–Cu^{2+}-clay complexes may also apply to the other FA–clay complexes, but this requires further verification.

CONCLUDING COMMENTS

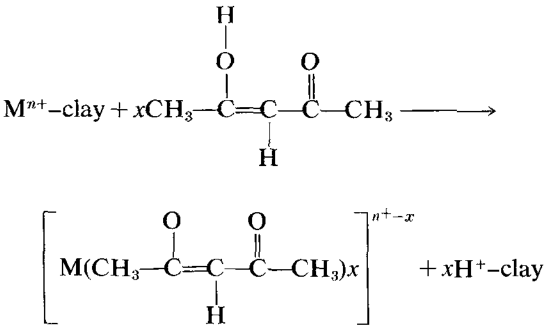
Previous investigations have indicated that in aqueous solutions, in the absence of clay, FA reacts with di- and tri-valent metal ions by two types of reactions to form stable complexes: (a) a

Table 5. Major bands in i.r. spectra of FA–clay complexes saturated with different cations and prepared at pH3·5

Saturating cation	cm^{-1}	RI	cm^{-1}	RI	cm^{-1}	RI	cm^{-1}	RI	cm^{-1}	RI	cm^{-1}	RI
Ag^{1+}	1850	14	1720	100	1620	172			1470	12	1430	55
Au^{1+}	1850	13	1720	100	1620	182			1455	5	1430	65
NH_4^{1+}	1850	14	1725	100	1620	145					1425	87
Cd^{2+}	1850	22	1725	100	1620	217			1460	9	1425	74
Co^{2+}	1850	16	1725	100	1620	182			1465	4	1430	64
Cu^{2+}	1850	25	1725	100	1625	145	1525	35			1425	46
Mg^{2+}	1850	17	1725	100	1625	244			1640	10	1430	73
Mn^{2+}	1850	12	1725	100	1620	233			1470	21	1420	79
Ni^{2+}	1850	16	1720	100	1625	200			1460	16	1430	56
Pb^{2+}	1850	12	1730	100	1620	204			1465	10	1425	73
Sn^{2+}	1850	12	1720	100	1620	170			1460	10	1430	76
Zn^{2+}	1850	14	1725	100	1620	175			1465	16	1425	47
Al^{3+}	1850	13	1720	100	1620	164	1520	7			1425	98
Cr^{3+}	1830	74	1700	100	1600	286			1465	57	1400	197
Fe^{3+}	1850	12	1720	100	1625	170			1460	12	1430	47

major one, involving simultaneously both acidic CO_2H and phenolic OH groups, and (b) a minor one, in which only less acidic CO_2H groups participate (Schnitzer and Skinner, 1965a; Gamble *et al.*, 1970). Water-soluble complexes are usually formed if molear metal/FA ratios are 1 : 1 or less, but if the ratios exceed 1 : 1, the complexes become water-insoluble (Schnitzer, 1971).

The results reported herein show that on clay surfaces and in interlamellar layers the reaction between FA and Cu^{2+} (and possibly also with most of the other metal ions) is different in that it also involves β-diketone groups in the FA to form chelates which are similar to acetylacetonates. These complexes are insoluble in water. It appears that montmorillonite affects the conformation of the FA polymer in a manner that favours reactions between C=O groups in the FA and metal ions. We have so far been unable to observe this type of reaction in aqueous solutions in the absence of clay. Parfitt and Mortland (1968) suggest that the reaction between acetylacetone and Cu^{2+}– and Al^{3+}-montmorillonite proceeds in the following manner:



$$M^{n+}\text{-clay} + x\mathrm{CH_3}{-}\overset{\overset{\text{H}}{|}\atop{\overset{\text{O}}{|}}}{\mathrm{C}}{=}\underset{\underset{\text{H}}{|}}{\mathrm{C}}{-}\overset{\overset{\text{O}}{\|}}{\mathrm{C}}{-}\mathrm{CH_3} \longrightarrow \left[\mathrm{M}(\mathrm{CH_3}{-}\overset{\overset{\text{O}}{|}}{\mathrm{C}}{=}\underset{\underset{\text{H}}{|}}{\mathrm{C}}{-}\overset{\overset{\text{O}}{\|}}{\mathrm{C}}{-}\mathrm{CH_3})x\right]^{n+-x} + xH^+\text{-clay}$$

Thus, the acetylacetone donates protons to the clay which results in the formation of H^+–clay, while the metal is complexed by the acetylacetone in the clay interlayer to form, depending on the number of protons released, either positively charged or neutral chelates.

Other reaction mechanisms proposed by Parfitt and Mortland (1968) include: (a) direct ion-dipole interaction of the C=O groups with metal ions that have low hydration energies, and (b) outer sphere coordination of C=O groups to metal ions by bridging through directly coordinated water molecules. Which of the three mechanisms applied to the FA–C=O–Cu^{2+}-montmorillonite interaction in the interlayer spaces awaits further investigation.

While we have focused much attention on reactions between β-diketone groups and metal ions, especially Cu^{2+} and Al^{3+} in and on the clay, our data also show the involvement of FA-COO^- groups. The reaction of COO^- groups with metal ions is likely to be most prominent on the outer clay surfaces. This reaction appears to be of the ligand-exchange type, involving incorporation of the FA-COO^- groups into the coordination shell of metal atoms at the clay surface (Greenland, 1971), since leaching with 1 N NaCl solution does not displace the FA from the clay. Other adsorption mechanisms that may be involved are hydrogen bonding and van der Waals forces. Whereas the exact reaction mechanism is not known at this time, our data show that FA can interact with clay minerals via C=O and COO^- groups to form complexes of considerable chemical stability. The formation of such complexes is, at least in part, responsible for the observed longevity of humic substances in soils and waters.

Acknowledgements—We thank J. G. Desjardins, G. C. Scott, M. Jaakkimainen and N. Miles for technical assistance.

REFERENCES

Allaway, W. H. (1949) Differential thermal analysis of clays treated with organic cations as an aid in the study of soil colloids: *Soil Sci. Soc. Amer. Proc.* **13**, 183.

Bradley, W. F. and Grim, R. (1948) Colloid properties of layer silicates: *J. Phys. Coll. Chem.* **52**, 1404.

Gamble, D., Schnitzer, M. and Hoffman, I. (1970) Cu^{2+}–fulvic acid chelation equilibrium in 0·1 M KCl at 25·0°C: *Can. J. Chem.* **48**, 3197.

Greenland, D. J. (1965) Interaction between clays and organic compounds in soils: II. *Soils and Fertilizers* **28**, 521.

Greenland, D. J. (1971) Interactions between humic and fulvic acids and clays: *Soil Sci.* **111**, 34.

Kodama, H. and Schnitzer, M. (1968) Effects of interlayer cations on the adsorption of a soil humic compound by montmorillonite: *Soil Sci.* **106**, 73.

Kodama, H. and Schnitzer, M. (1969) Thermal analysis of a fulvic acid-montmorillonite complex: *Proc. Intern. Clay Conf., Tokyo* **1**, 765.

Kodama, H. and Schnitzer, M. (1971) Evidence for interlamellar adsorption of organic matter by clay in a Podzol soil: *Can. J. Soil Sci.* **51**, 509.

Martell, A. E. and Calvin, M. (1952) *Chemistry of metal chelate compounds*: Prentice-Hall, N.J.

Mortland, M. M. (1970) Clay-organic complexes and interactions: *Advances in Agronomy* **22**, 75.

Nakamoto, K. (1963) *Infrared spectra of inorganic and coordination compounds*: John Wiley, N.Y.

Ortiz de Serra, M. I. and Schnitzer, M. (1972) The chemistry of humic and fulvic acids extracted from Argentine soils. II. The alkaline permanganate oxidation of methylated humic and fulvic acids: *Soil Biol. Biochem.* (In press).

Parfitt, R. L. and Mortland, M. M. (1968) Ketone adsorptions on montmorillonite: *Soil Sci. Soc. Amer. Proc.* **32**, 355.

Schnitzer, M. (1971) Metal-organic matter interactions in soils and waters. In "*Organic Compounds in Aquatic Environments*": (Editors S. J. Faust and J. V. Hunter). Marcel Dekker.

Schnitzer, M. and Hansen, E. H. (1970) Organo-metallic interactions in soils. 8: An evaluation of methods for the determination of stability constants of metal-fulvic acid complexes: *Soil Sci.* **109**, 333.

Schnitzer, M. and Kodama, H. (1966) Montmorillonite: effect of pH on its adoption of a soil humic compound: *Science* **153**, 70.

Schnitzer, M. and Kodama, H. (1967) Reactions between a Podzol fulvic acid and Na-montmorillonite: *Soil Sci. Soc. Amer. Proc.* **31**, 632.

Schnitzer, M. and Riffaldi, R. (1972) The determination of quinone groups in humic substances: *Soil Sci. Soc. Amer. Proc.* (In press).

Schnitzer, M. and Skinner, S. I. M. (1963) Organo-metallic interactions in soils: 1. Reactions between a number of metal ions and the organic matter of a Podzol Bh horizon: *Soil Sci.* **96**, 86.

Schnitzer, M. and Skinner, S. I. M. (1965a) Organo-metallic interactions in soils: 4. Carboxyl and hydroxyl groups in organic matter and metal retention: *Soil Sci.* **99**, 278.

Schnitzer, M. and Skinner, S. I. M. (1965b) The carbonyl group in a soil organic matter preparation: *Soil Sci. Soc. Amer. Proc.* **29**, 400.

Talibudeen, O. (1952) The technique of differential thermal analysis (DTA). 1: *J. Soil Sci.* **3**, 251.

Résumé—Le fait d'agiter à pH 2,5 une montmorillonite Cu^{2+} en présence d'acide fulvique soluble dans l'eau fait passer l'espacement interlamellaire de 10,0 à 15,1 Å. Les espacements sont mesurés à une humidité relative ≈ 0%. L'intensité de l'adsorption interfeuillet décroît quand le pH augmente. Les analyses thermique différentielle et thermogravimétrique montrent qu'en plus de l'adsorption interfeuillet, l'acide fulvique est retenu également sur les surfaces externes de l'argile. L'acide fulvique est si fortement retenu par l'argile Cu^{2+} que plus des $\frac{3}{4}$ de la quantité totale adsorbée, incluant les produits de dégradation auxquels elle donne naissance, résistent à la décomposition même lors d'un chauffage à 1000°C. Les spectres i.r. montrent que les groupes β-dicétone de l'acide fulvique réagissent avec les ions Cu^{2+} présents dans ou sur l'argile en donnant des chélates du type acétylacétonate. Certains résultats indiquent que le mécanisme postulé pour l'interaction acide fulvique-Cu^{2+}-argile peut aussi s'appliquer aux réactions entre l'acide fulvique et la montmorillonite saturée par d'autres cations di ou trivalents. Les réactions entre les solutions aqueuses d'acide fulvique et les cations en présence d'argile diffèrent de celles qui s'établissent en l'absence d'argile. La montmorillonite semble affecter la conformation du polymère acide fulvique d'une manière qui favorise les réactions entre les groupes C=O et les cations, ce qui constitue un type de réaction qui n'avait pas encore été observé en solution aquese en l'absence d'argile.

Kurzreferat—Schütteln von wasserlöslicher Fulvinsäure mit Cu^{2+}–Montmorillonit bei pH 2,5 erhöhte den Lamellarabstand von 10,0 auf 15,1 Å. Die Abstände wurden bei ≈ 0% relativer Feuchtigkeit gemessen. Das Ausmass an Zwischenschichtenadsorption nahm ab mit zunehmendem pH. Differentielle thermische Analyse und thermogravimetrische Untersuchungen zeigten, dass neben Zwischenschichtenadsorption, die Fulvinsäure auch auf äusseren Tonoberflächen aufgenommen wurde. Die Fulvinsäure wurde durch den Cu^{2+}-Ton so fest gehalten, dass $> \frac{3}{4}$ der adsorbierten Gesamtmenge, einschliesslich der daraus gebildeten Abbauprodukte, sogar bei Erhitzung bis auf 1000°C, der Zersetzung widerstanden. Ultrarot-Spektren zeigten, dass β-Diketongruppen in der

Fulvinsäure mit Cu^{2+} in oder auf dem Ton reagierten unter Bildung von Chelaten vom Azetylazetonat Typ. Es wurden Anzeichen dafür erhalten, dass der für die wechselseitige Fulvinsäure-Cu^{2+}–Ton Reaktion vorgeschlagene Mechanismus auch auf Reaktionen zwischen Fulvinsäure und Montmorillonit gesättigt mit anderen zwei- und dreiwertigen Metallionen anwendbar ist. Reaktionen von Fulvinsäure in wässrigen Lösungen mit Metallionen in Anwesenheit von Tonen unterscheiden sich von denen in der Abwesenheit von Ton. Es scheint, dass Montmorillonit die Conformation des Fulvinsäure Polymers in einer Weise beeinflusst, die Reaktionen zwischen C=O Gruppen und Metallionen begünstigt, eine Art von Reaktion, die bisher in wässrigen Lösungen in der Abwesenheit von Ton nicht beobachtet worden ist.

Резюме — Встряхивание водорастворимой фульвиновой кислоты с Cu^{2+}–монтмориллонитом при pH 2,5 повысило межпластинчатый параметр от 10,0 до 15,1 А. Параметры измерялись при $\approx 0\%$-ой относительной влажности. Степень межслойной адсорбции понизилась с увеличением pH. Дифференциальный термоанализ и термогравиметрические исследования показали, что дополнительно к межслойной адсорбции, фульвиновая кислота также удерживалась на наружной поверхности глины. FA удерживалась так сильно глиной Cu^{2+}, что $>3/4$ общего адсорбированного количества, включая продукты деградации от нее, сопротивлялись разложению даже при подогреве до 1000°C. Инфракрасный спектр показал, что β-дикетоновые группы фульвиновой кислоты реагировали на Cu^{2+} в глине или на ней для формирования клешней ацетилацетонатового типа. Нашли индикации, что механизм постулированный для взаимодействия FA-Cu^{2+}–глины может также относиться к реакции между FA и монтмориллонитом, насыщенным другими ди- и тривалентными металлическими ионами. Реакция FA в водных растворах на металлические ионы в присутствии глины, отличается от реакции происходящей в ее отсутствии. Очевидно, монтмориллонит влияет на конформацию полимера фульвиновой кислоты так, что поощряется реакция между группами C=O и металлическими ионами, этот тип реакции до сих пор еще не наблюдался в водных растворах в отсутствии глины.