

THE INFRARED SPECTRA OF VALINE ADSORBED ON Cu-MONTMORILLONITE¹

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ABSTRACT

The infrared spectra (4000-1200 cm^{-1}) are obtained for several Cu-montmorillonite-valine complexes that have been prepared at several different pH values. Analysis of the spectra indicates the presence in the interlamellar spaces of both a bidentate chelate complex and a monodentate complex in which a Cu^{2+} -ion is coordinated to the N-atom of the amino acid. The relative concentrations of these adsorbed species in the clays are pH dependent. Possible trace amounts of valinium cations are detected when the preparation pH is below 3.0.

INTRODUCTION

Infrared spectroscopy can effectively determine the structures of many compounds adsorbed on clays. Cloos *et al.* (1956) have investigated the infrared spectra of various amino acids adsorbed on sodium-, calcium-, and hydrogen-montmorillonite, and determined that the protonated cation was the dominant adsorbed species. In this investigation, we have analyzed the infrared spectra of valine adsorbed on copper-montmorillonite at several different pH's to determine whether copper-amino acid complexes can be detected in the interlamellar spaces. The infrared spectra of related complexes in crystals have been used to identify the adsorbed species, and to make empirical band assignments.

EXPERIMENTAL

A. Preparation of Clay Films

The montmorillonite used in this study originated from Wyoming. Clay films were prepared from clay particles whose equivalent diameters were less than two microns. Cu-montmorillonite was obtained by saturating natural clay with a 1N CuCl_2 solution. The clay had to be washed several times with distilled water to eliminate free Cu^{2+} ions. H-montmorillonite was prepared immediately prior to use from a 1 percent suspension of natural clay by passing it through a column of Amberlite IR-120 (H-form).

Equal amounts of the appropriate clay suspension and a 0.05 M aqueous solu-

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tion of valine (K & K Laboratories, Inc.) were mixed together. The pH of the mixture was measured and adjusted to the appropriate value by adding 0.1 N hydrochloric acid or sodium hydroxide solution. The resulting suspension was mechanically shaken overnight. The clay-valine complex was separated from the supernatant by centrifuging at 18,000 rev./min. at 20°C for one hour using a Sorvell Superspeed RS-2B Automatic Refrigerated Centrifuge. The supernatant was decanted off, and the clay complex was redispersed in 10 ml of distilled water by vigorous shaking. The clay complex was again separated from the resulting supernatant by centrifugation and decantation. This clay sample was redispersed in 10 ml of distilled water to be used in the preparation of the films. Self-supporting thin films (approximately one-inch diameter, 2-4 mg/cm²) were prepared by evaporating 2 ml of the clay complex-distilled water suspensions on an aluminum foil supported by a flat glass plate. Since most exchangeable cations react with aluminum foil, the foil had to be lined with a thin film of collodion to protect the clay from chemical reactions. The specimens were dried over P₂O₅ in a slightly evacuated desiccator. The resulting dried film specimens were easily stripped from the foil by drawing the foil over a sharp edge. X-ray diffraction analysis indicated that valine formed single-layer complexes in the clays. The basal spacings of the clay-valine complexes ($d_{001} = 13.2 \text{ \AA}$ and $d_{004} = 3.3 \text{ \AA}$) are slightly larger than those of either the glycine or the α -alanine complexes. This is expected because of the larger number of methyl groups attached to the methylene carbon atom in valine.

B. Infrared Studies

The infrared adsorption spectra (4000 — 1200 cm⁻¹) were obtained for each clay specimen by placing their corresponding self-supporting thin films in the sample beam of a Perkin-Elmer Model 621 double-beam grating spectrophotometer. The use of clay films prepared from clay particles whose equivalent diameters were less than two microns minimized the scattering perturbations on spectra due to the Christiansen effect. The self-supporting films were sufficiently thin so that highly resolved spectra could be obtained with slight attenuation of the reference beam. An air purging unit was employed to eliminate adsorption bands due to atmospheric water and carbon dioxide. Calibration of the spectrophotometer was carried out using polystyrene bands and a wavenumber accuracy of $\pm 3 \text{ cm}^{-1}$ was obtained.

RESULTS AND DISCUSSION

The infrared spectra of H- and Cu-montmorillonite complexes containing intercalated valine that were prepared at several different pH's are shown in Figure 1. A strong band at *ca.* 3630 cm⁻¹ is due to the lattice hydroxyl stretching mode for montmorillonite. Band assignments for the valine-montmorillonite complexes are made by using the band assignments obtained by Nakagawa *et al.* (1965) for the valine zwitterion and its copper chelated complex in crystals. The observed wavenumbers and their band assignments are listed in Table 1.

In the upper region of the spectra, the observed wavenumbers *ca.* 3340 and 3270 cm⁻¹ for Cu-montmorillonite-valine complexes pre-

pared at pH 5.6 are assigned to NH stretching modes. Cu-clay complexes prepared at pH's less or greater than this pH value do not show sufficiently strong bands in this region because the amount of amino acid adsorbed on the clay is very low. However, for the sample prepared at a pH of 5.6, the wavenumbers of the NH stretching modes indicate that the amino group is coordinated to the Cu^{2+} ion. For the H-clay complex, the NH stretching modes appear at 3220 and 3180 cm^{-1} indicating the presence of a NH_3^+ group on the amino acid adsorbed on the clay. The bands at 1615, 1570, 1465, and 1417 cm^{-1} for the Cu-clay complex (pH 5.6) can be readily assigned to the carboxyl asymmetric stretching, the NH_2 bending, the CH_3

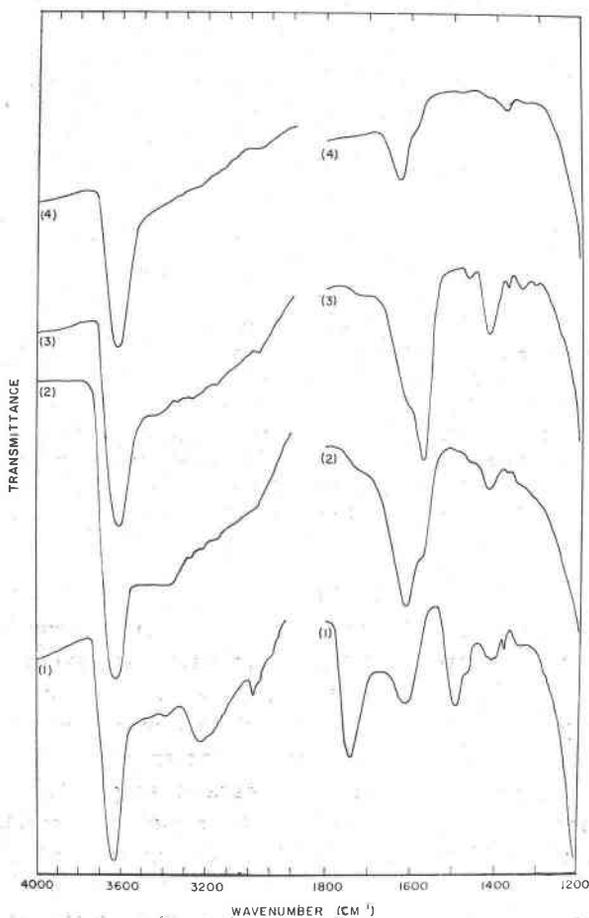
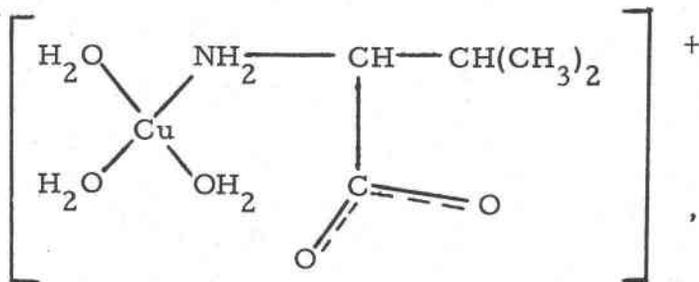


FIG. 1. The Infrared spectra of valine complexes with (1) R-montmorillonite and (2)–(4) Cu-montmorillonite: Equilibrium pH's (2) 2.9, (3) 5.6, and (4) 8.2.

Table 1. Band Assignments of Valine-Montmorillonite Complexes Prepared at Several Different pH Values.

Nakagawa et al. (1965)		Cu-clay Complexes			H-clay Complex	Assignments
Zwitterion	Cu-complex	pH 2.9	5.6	8.2	2.9	
	3297		3345			NH ₂ asym. str.
	3250		3275			NH ₂ ⁺ sym. str.
3132					3220(m, b)	NH ₃ ⁺ str.
2989	2986				3180(sh)	CH str.
2884	2876		ca. 2960(b)		ca. 2970(w)	COOH str.
1627(sh)		1730(vw)			1742(s)	NH ₃ ⁺ deg. def.
1596(s)	1610(s)	1615(s, b)	1615(sh)	1630(s)	1610(s)	COO ⁻ asym. str.
	1583(sh)					NH ₂ bend.
	1572(sh)	1570(sh)	1570(s)	1590(sh)		NH ₃ ⁺ sym. def.
1500					1492(s)	
1469	1466	1465	1465	1465	1465(sh)	CH ₃ deg. def.
	1455				1410	CO ⁻ str. plus OH bend.
1411	1381(s)	1417(m)	1417(m)	1376		COO ⁻ sym. str.
1389						CH ₃ sym. def.
1364	1370(sh)	1375(vw)	1375(w)		1380(w)	CH bend.
1356	1352	1340	1340		1350	(coupled with NH ₂ wagg. for Cu)
1324	1326	1310	1310	1310		
1317	1309					
1269	1277					

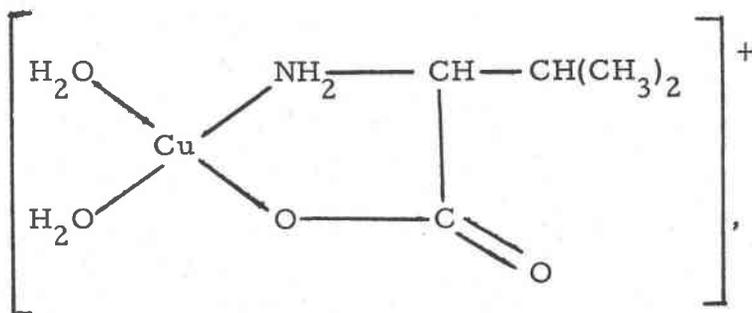
degenerate deformation, and the carboxyl symmetric stretching modes. Comparing the wavenumbers of the asymmetric and the symmetric carboxyl stretching modes of the intercalated amino acid complexes prepared at pH 5.6 or lower with those of the zwitterion and the chelated complex leads to the conclusion that the carboxyl group is free and ionized similarly to the glycine and α -alanine complexes prepared at comparable pH values. Therefore, it appears that the monodendate copper complex,



is the dominant species adsorbed for the clay complexes prepared at pH of 5.6 or lower. The wavenumbers observed for these complexes below 1400 cm^{-1} may be assigned to the CH bending mode.

The observed bands at 1630 and 1376 cm^{-1} in the spectrum for the Cu-clay complex prepared at pH 8.2 can be assigned to the carboxyl asymmetric and symmetric stretching modes. These wavenumbers

are very close to those observed for the copper chelate complex with valine in crystals,



indicating that formation of this complex in Cu-montmorillonite is favored at high preparation pH's. Since the above Cu-complexes have single charges and the Cu-ion has a double charge, the exchange capacity of the clay must be balanced by the H⁺-ions liberated from valine.

Band assignments are made in Table 1 for the valinium cation adsorbed on H-montmorillonite. A strong band at 1742 cm⁻¹ is assigned to the CO stretching mode of the COOH-group. The spectrum of Cu-clay-valine complex prepared at a pH value of 2.9 shows a weak shoulder at 1730 cm⁻¹. This band indicated the possible presence of a trace amount of the cationic species in the clay.

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