Surface and Intercalate Chemistry of Layered Silicates. Part II.¹ An Iron-57 Mössbauer Study of the Role of Lattice-substituted Iron in the **Benzidine Blue Reaction of Montmorillonite**

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Direct ⁵⁷Fe-Mössbauer-spectroscopic evidence is presented for the involvement of lattice-subsituted iron(III) as an electron-accepting site, within montmorillonite, following intercalation of the clay by benzidine which results in the production of benzidine radical cations. The subsequent oxidation of the resulting iron(1), by dehydration of the benzidine blue-montmorillonite intercalate, is explained in terms of two simple equilibria which are set up at the clay surfaces. New Lewis-acid sites [involving iron(III)], created by oxidation of the original (ironII) ions in the clay, have been found to be active even under conditions where it is expected that benzidine species are present only at external surfaces of the montmorillonite.

BENZIDINE reacts with the layered-sheet aluminosilicate clay mineral montmorillonite, in the presence of water, to produce a blue colour,²⁻⁴ the intensity of which is a

¹ Part I, D. T. B. Tennakoon, J. M. Thomas, M. J. Tricker, and J. O. Williams, preceding paper. ² A. Hakusui, Y. Matsunaga, and K. Kmehara, *Bull. Chem.*

Soc. Japan, 1968, 7, 389.

function of the exact nature of the clay mineral and its previous history. If the blue material is dehydrated, a yellow-green complex results: these processes are

³ E. A. Hauser and M. B. Leggett, J. Amer. Chem. Soc., 1940, 62, 1811.
⁴ S. B. Hendricks and L. T. Alexander, J. Amer. Agron. Soc.,

1940, 32, 455.

reversible to the addition or removal of water.^{2,5-9} Diffuse-reflectance studies 2,7-9 of systems of benzidinebentonite (a mineral closely akin to montmorillonite) have established that the blue colouration is produced by oxidation of benzidine (bzn) yielding monovalent radical cations (bzn⁺) which are present as isolated, or as interacting aggregates of, radical cations depending on the degree of wetting by the solvent.² There is confusion, however, as to the reason for the loss of the blue, and for the production of the yellow, material on dehydration. Dodd and Ray suggested 10 that the yellow colouration arises as a result of formation of the divalent ' semiquinone' cation (Hbzn²⁺) as surfaces of dry montmorillonite are known to be acidic 11 [equation (1)].



However the more recent work of Hakusui et al.,² and in these laboratories, suggests that the yellow colour arises from formation of the bivalent radical cation (bzn^{2+}) and monoprotonated benzidine (Hbzn⁺) from a pair of monovalent benzidine radical cations at the clay surface [equation (2)].

$$2bzn^+ + H^+ \stackrel{dry}{\Longrightarrow} bzn^{2+} + Hbzn^+$$
 (2)

The nature of the electron-acceptor sites on the clay surface have been recently reviewed by Theng 12 and discussed by Solomon et al.,⁵ who observed that clays with high iron(III) ion concentrations (either as a result of natural causes or by chemical oxidation with, for example, hydrogen peroxide) gave intense blue colourations and that reduced clays yielded only a pale colour on addition of benzidine. Furthermore, it was previously noted that reduced montmorillonites treated with polyphosphates, which are specifically adsorbed on edge sites,¹³ gave only slight colouration. It was therefore concluded 5 that the electron-acceptor sites on the clay were either (a) iron(III) ions at the planar surfaces and/or (b) aluminium atoms exposed at crystal edges. Conflicting reports also exist as to the effect of dioxygen on the reaction. A number of workers 3,4 found no change in the intensity of the blue colour,⁵ whereas others observed that the presence of dioxygen increases the ease at which the mineral can oxidize benzidine.

As ⁵⁷Fe Mössbauer spectroscopy allows a direct probe of the oxidation state of iron within materials such as montmorillonite, a study of one of the proposed Lewisacid sites in the oxidation of benzidine should provide unambiguous direct evidence as to whether or not

⁶ E. J. Kotoo, Optics and Spectroscopy, 1956, 1, 500.
⁷ Y. Matsunaga, Bull. Chem. Soc. Japan, 1972, 45, 770.
⁸ H. Takanashi, Bull. Chem. Soc. Japan, 1955, 28, 5.
⁹ N. Lahav, Israel J. Chem., 1972, 10, 925.
¹⁰ C. G. Dodd and S. Ray, Clays and Clay Minerals, 1960, 8, 237.

structural iron is involved in these reactions. Lewisacid sites are expected to be of importance in phenomena such as the catalytic activity of montmorillonite. In the preceding paper we discussed the quantitative uptake of benzidine by aqueous dispersions of montmorillonite. Two regimes were clearly identified: pre- and postintercalation. We report here a ⁵⁷Fe Mössbauer study of pre- and post-intercalated samples and also on the effect of treating the original montmorillonite with hydrogen peroxide.

RESULTS AND DISCUSSION

The Mössbauer Spectrum of Montmorillonite.-The Mössbauer spectrum of Wyoming montmorillonite is shown in Figure (a) and the related parameters for this and other materials are summarized in Table 1. The spectrum of original montmorillonite clearly shows the presence of both iron(II) and iron(III), the low-energy shoulder and the resonance at high energy being assignable to the presence of high-spin iron(II), and the low-energy doublet corresponding to iron(III). The iron(II) : iron(III) ratio was ca. 0.16 : 1 assuming that the recoil-free fraction at all iron sites is the same. The idealized structure of montmorillonite 14,15 (see Figures 1 and 2 of preceding paper) consists of aluminosilicate layers made up from an infinite network of silica tetrahedra which are bonded via bridging oxygen atoms at the base of the tetrahedra leading to sheets of general composition $[\mathrm{Si}_4\mathrm{O}_{10}]^{4-}.$ In so far as the sequence is tetrahedral-octahedral-tetrahedral, the structure of montmorillonite is analogous to that of biotite.

In montmorillonite (which is dioctahedral) two thirds, and in biotite (which is trioctahedral) all, of the potentially octahedral sites between the [Si₄O₁₀]⁴⁻ units are filled by trivalent cations which are predominantly aluminium, the six-co-ordination of aluminium being completed by two bridging hydroxo-groups. Two possible types of co-ordination of the trivalent cation result: one with cis- and one with trans-hydroxo-groups, denoted M1 and M2 respectively. The M1 : M2 site ratio is 2:1 and in a dioctahedral clay cation repulsions are minimized by preferential occupation of the M1 sites. Three possible sites therefore (M1, M2, and a tetrahedral one) are present in montmorillonite for substitution by iron. The Mössbauer spectrum was initially computerfitted assuming two sites, an iron(II) and iron(III) quadrupole doublet. Peaks of the iron(II) doublet (Table 1) had a narrow linewidth of 0.26 mm s⁻¹ $(\pm 0.01 \text{ mm s}^{-1})$ close to natural {the ⁵⁷Co-Pd source used with a thin Na2[Fe(CN)5NO] absorber gave a full linewidth of 0.28 mm s⁻¹ (± 0.01 mm s⁻¹)} suggesting

- ¹³ A. S. Michaels, *Ind. and Eng. Chem.*, 1958, **50**, 1951.
 ¹⁴ G. W. Brindley in 'X-Ray Identification and Crystal Structures of Clay Minerals,' Mineralogical Society, London, 1951,
- p. 89. ¹⁵ R. E. Grim, 'Clay Mineralogy,' McGraw-Hill, New York, 1968.

⁵ D. H. Solomon, B. C. Loft, and J. D. Swift, Clay Minerals, 1968, 7, 389.

¹¹ J. Fripiart, Trans. 8th Internat. Congress Soil Sci., Bucharest, 1964, **1**, 171.

¹² B. K. G. Theng, Clays and Clay Minerals, 1971, 19, 383.



Velocity/mm s⁻¹

⁵⁷Fe Mössbauer spectrum of (a) a natural montmorillonite from Upton, Wymong, containing ca. 4% by weight of total iron [Note th presence of both iron(11) and iron(111) within the clay.]; (b) montmorillonite following oxidation with hydrogen peroxide; (c) a benzidine blue-montmorillonite complex prepared in the post-intercalation regime [Note enhancement of the intensity of the iron(11) doublet relative to the original clay mineral in (a).]; and (d) montmorillonite following treatment with hydrazine

TABLE 1

Mössbauer parameters observed in this work for montmorillonite-benzidine systems. Isomer shifts (δ) {relative to $Na_2[Fc(CN)_5NO]$ }, quadrupole splittings (Δ), and full widths at half maxima (f.w.h.m.) are in mm s⁻¹ (± 0.01 mm s⁻¹). Pre-intercalated blue samples, thoroughly dehydrated post-intercalated samples, and moist blue samples of the oxidized clay had spectra virtually superimposible with that of the original montmorillonite

	Fe ²⁺			Fe^{3+}			
Material	8	Δ	F.w.h.m.	8	Δ	F.w.h.m.	Fe ²⁺ : Fe ³⁺
Montmorillonite	1.36	2.78	0.26	0.61	0.63	0.68	0.16:1
Representative moist intercalated benzidine blue-montmorillonite	1.36	2.77	0.28	0.29	0.62	0.70	0·41 : 1
Hydrogen peroxide-treated montmorillonite				0.60	0.64	0.58	0
Hydrazine-treated montmorillonite	1.36	2.69	0.29	0.58	0.70	0.51	2.47:1

preferential occupation of one site by Fe^{2+} . The isomer shift and quadrupole splitting (Table 1) were typical of high-spin iron(II) ion in a six-co-ordinate environment



and were similar to those assigned to the M1 site of biotites ¹⁶ (Table 2). The parameters of iron(III)

TABLE 2

Literature values and assignments for Mössbauer parameters (mm s⁻¹) of biotites {isomer shifts relative to $Na_{2}[Fe(CN)_{5}NO]$. The assignments of Fe^{2+} are based on the arguments of ref. 16. See ref. 17 for further details

			Δ		
Ion	Site	δ	mm s ⁻¹	F.w.h.m.	Ref.
Fe^{2+}	Ml	1.32	2.14	0.40	19
		1.36	2.18		16
		1.30	2.02	0.20	18
	M2	1.33	2.58	0.20	19
		1.39	2.61	0.46	20
		1.39	$2 \cdot 56$		16
Fe ³⁺	M1 and M2	0.65	0.72	0.46	19
		0.73	0.67	0.42	20
		0.807	0.55		16
		0.66	0.67	0.40	18
	M1	0.69	0.91	0.36	18
	M2	0.68	0.52	0.28	

again indicate a distorted six-co-ordinate immediate oxygen environment. However, the linewidths of the quadrupole doublet were considerably larger than those of iron(II) and one suspects that the smaller iron(III) ion may be distributed over both M1 and M2, the parameters for which are expected to be similar (Table 2). Attempts to fit two iron(III) sites to the central doublet were, however, unsuccessful, the parameters probably being too close to permit resolution. Moreover, random substitution would increase the number of sites resulting in an overlapping pattern of many similar doublets.

In the purification of the clay minerals (see Experimental section) efforts were made, for reasons outlined later, not to oxidize further the iron(II) content of the mineral. The normal geological practice of treatment with H_2O_2 (to remove organic matter), or boiling colloidal suspensions (to assist flocculation after initial sedimentation), resulted in oxidation of all the iron(II) ions. The spectrum of a hydrogen peroxide-treated clay is shown in Figure (b) and it can be seen that the iron(II) content of the clay mineral has disappeared.

¹⁶ L. Häggstrom, R. Wäppling, and H. Annersten, Chem. Phys. Letters, 1969, 4, 107.

448. ¹⁸ N. J. Yassoglou, C. Nobeli, A. J. Kostikas, and A. C. Simo-poulas, Soil Sci. Soc. Amer. Proc., 1972, **36**, 520.

Mössbauer Spectra of Pre- and Post-intercalated Benzidine-Montmorillonite Complexes.-Typical Mössbauer spectra of pre-intercalated benzidine blue complexes were essentially the same as those of the original clay, and it is clear that there is no significant increase in the iron(II) content at the expense of iron(III). However, spectra [Figure (c)] of blue samples prepared from the post-intercalation regime showed a considerable enhancement of iron(II) at the expense of iron(III) content of the clay, and the iron(II) doublet had similar parameters (Table 1) to those of the original iron(II) content. [Linewidths of the iron(II) doublet remained small and attempts to fit two iron(II) sites were unsuccessful.] Vacuum dehydration of these led to disappearance of this increased iron(II) signal but the Fe^{2+} : Fe^{3+} ratio never became smaller than that of the original montmorillonite. The iron(III) produced had similar parameters (Table 1) to the original iron(III) content. Exposure of the yellow complex to moisture resulted in regeneration of iron(II), the Fe²⁺: Fe³⁺ ratio being dependent on the degree of moistening.

Reversible oxidation-reduction of iron by moist dioxygen has been previously observed for iron(II)exchanged Y-zeolites.^{21,22} However, similar control experiments at room temperature on montmorillonite showed no change in the Fe^{2+} : Fe^{3+} ratio. Clearly the blue-to-yellow transformation involves reversible oxidation-reduction of the structural iron content of the montmorillonite in the presence of benzidine in a process which involves electron transfer across the aluminosilicate layer boundary, and no major changes, detectable by Mössbauer spectroscopy, appear to occur in the structural environment of the iron. The basic aluminosilicate layer structure is preserved during the benzidine blue reaction.

Mössbauer Spectra of the Oxidized Montmorillonite-Benzidine Complex.—The intensity of the blue colouration produced by the action of benzidine was found to be greater if the clay was first treated with hydrogen peroxide.⁵ Spectra of benzidine blue derivatives of oxidized clays containing only iron(III) (see below), prepared under conditions not expected to lead to intercalation, showed regeneration of the iron(II) content of the clay but they still retained a large proportion of iron(III). It was possible to execute a similar oxidation-reduction process on dehydration and moistening, but the Fe²⁺ : Fe³⁺ ratio never exceeded that of the original clay and it was possible to convert all the iron(11) to iron(III) on dehydration.

Conclusions.—The Mössbauer spectroscopic study clearly shows that iron(III) functions as an electronacceptor site under certain circumstances. Moreover a number of additional points are raised by our observations: (a) the difference in behaviour of benzidine blue

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 R. L. Garten, W. N. Delgass, and M. Boredart, *J. Catalysis*,
- 1970, **18**, 90.
- ²² J. A. Morice and L. V. C. Rees, Trans. Faraday Soc., 1968, **64**, 1388.

¹⁷ B. A. Goodman and M. J. Wilson, *Mineral. Mag.*, 1973, **39**,

¹⁹ C. S. Hogg and R. E. Meads, Mineral. Mag., 1970, 37, 606.

complexes prepared in a manner corresponding to preand post-intercalation; (b) the hitherto undetected oxidation, on dehydration, of the iron(II) produced as a consequence of formation of the blue radical, and the general role of water in the reaction; (c) the apparent generation of a new Lewis-acid site by oxidation of the iron(II) content of the clay on treatment with hydrogen peroxide.

That sufficient benzidine had been added to the oxidized clay to produce a detectable change in the iron(II) : iron(III) ratio, suggests that iron(II) ions are produced only following intercalation of the original clay by benzidine and that most if not all of the active Lewis-acid sites are located at interior surfaces of the original montmorillonite, iron(III) at external surfaces being inactive. The observed reversible reduction of iron(III) can be explained in terms of equilibria (3) and (4).

$$bzn + Fe^{3+} \Longrightarrow bzn^+ + Fe^{2+}$$
(3)

$$bzn + H^+ \Longrightarrow Hbzn^+$$
 (4)

The initial reaction lies far to the right in moist conditions. However dehydration of the clay is known to produce acidic surfaces 11 (Brønsted-acid sites being produced by ionization of structural hydroxide groups and residual water molecules¹¹). Under these conditions many amines are protonated (see for instance the i.r. evidence for protonation of pyridine intercalated into dehydrated montmorillonites 23) and consequently free benzidine is removed by reaction (4) driving equilibrium (3) to the left, thereby producing iron(III) as observed by Mössbauer spectroscopy.* The structural implications of this scheme are not altogether clear. If we are to follow the analogy of biotite, the implication is that a fraction of the iron(III) irons are in one site and these alone are reduced to iron(II), since the Mössbauer parameters of iron(II) produced by reduction are close to those of the original iron(II) assumed to be in one site. Solomon⁵ suggested, from a consideration of the size of the iron(II) and iron(III) ions and the dimensions of the silicate lattice, that only a fraction of the octahedral iron(III) present is involved in the benzidine blue reaction, but our inability to achieve complete reduction of the iron(III) content may be limited by other factors.

* During more recent studies on the benzidine blue and other colour reactions of montmorillonite, we observed that iron(III) can be regenerated by addition of acid to the moist benzidine blue complex in accordance with the proposed equilibria.

 \dagger 1 eV \approx 1.60 \times 10⁻¹⁹ J.

It should be noted that complete reduction of the iron(III) content of Wyoming montmorillonite could not be achieved with hydrazine [Figure (d)]. These observations and interpretations do not rule out any other equilibria proposed by other workers ^{5,10} where the initial oxidation process may have occurred at Lewisacid sites other than those involving iron(II), which undoubtedly exist at the surfaces of montmorillonite.

More difficult to rationalize are the reactions of oxidized montmorillonites prepared under conditions where intercalation is not expected to occur. Studies²⁴ of the oxidation of the iron(II) content of biotites suggest that a possible oxidation mechanism results in ejection of iron in the form of an oxide or hydrated oxide from the lattice. Hydrogen-peroxide treatment of the montmorillonite may result in ejection and nucleation and subsequent growth of small particles of iron hydroxide oxides at the exterior surface of the clay particles, thus making this iron(III) accessible to benzidine even in the supposedly pre-intercalated samples.

EXPERIMENTAL

The purification procedure and characteristics of the montmorillonite used (total iron content ca. 4% by weight) were described in the preceding paper.

Mössbauer spectra were recorded using a Harwell Mössbauer spectrometer of the constant-acceleration type. Spectra of powdered samples (containing less than 10 mg cm⁻² of iron) were accumulated in a 256-channel analyser using a 10 mCi ⁵⁷CoPd source. The 14·4 keV γ -radiation was detected using a long Xe–CH₄ counter with a thin aluminium end window.[†] The spectrometer was calibrated with either an iron foil or an Na₂[Fe(CN)₅NO] adsorber. Spectra were numerically fitted assuming Lorentzian line shapes using an Algol 'least-squares' program on an ICL 4130 computer. χ^2 Tests were carried out on the resultant fits as a guide to goodness of fit. Mössbauer parameters are accurate to ± 0.01 mm s⁻¹.

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