Surface and Intercalate Chemistry of Layered Silicates. Part V.[1] Infrared, Ultraviolet, and Visible Spectroscopic Studies of Benzidine–Montmorillonite and Related Systems

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Clay minerals of the montmorillonite family provide a matrix on which radical cations of a variety of amines may be formed. The origin of the different colours associated with the benzidine (bzn)–, *NNN'N'*-tetramethylbenzidine (tbzn)–, and *trans*-4,4'-diaminostilbene (dsn)–montmorillonite complexes has been further elucidated by u.v. and visible reflectance and i.r. spectroscopy. It is established that both uni- and di-positive bzn radical cations and protonated bzn moieties can exist at the internal and external clay surfaces. This is in contrast to the situation which prevails for tbzn where only the unipositive radical cation and protonated moieties appear to be formed. The interaction of montmorillonite with dsn dihydrochloride is similar to that of bzn but the nature of the product is modified by the presence of protons in cation-exchange sites.

BENZIDINE reacts with montmorillonite, in the presence of water, to produce a blue material which reversibly yields a yellow or yellow-green material on dehydration.[2] In the first paper of this series we reported[3] that the interaction of *NNN'N'*-tetramethylbenzidine with montmorillonite produced a green complex and that this material was stable to mild dehydration. It was also noted that the interaction of *trans*-4,4'-diaminostilbene dihydrochloride with montmorillonite yielded a green complex which turned brown on dehydration and that the brown form was generally stable to rehydration.[3] In a previous study Matsunaga[4] concluded, by comparison of the u.v. and visible reflectance spectra of blue benzidine–montmorillonite complexes with those of solid salts of perchlorate derivatives of unipositively charged benzidine radical cations (bzn^+), that the blue colouration of the clay is attributable to these radicals interacting at the clay surfaces. The cause of the yellow colour is less well understood and controversy still surrounds its origin. Dodd and Ray[5] suggested that the yellow colour is due to a protonated unipositive benzidine radical cation. More recently, however, Matsunaga[4] has argued, by analogy to similar systems,

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[1] Part IV, J. M. Adams, J. M. Thomas, and M. J. Walters, *J.C.S. Dalton*, 1975, 1459.

[2] D. H. Solomon, B. C. Loft, and J. D. Swift, *Clay Minerals*, 1968, **7**, 389; N. Lahav, *Israel J. Chem.*, 1972, **10**, 925.

[3] D. T. B. Tennakoon, J. M. Thomas, M. J. Tricker, and J. O. Williams, *J.C.S. Dalton*, 1974, 2207.

[4] Y. Matsunaga, *Bull. Chem. Soc. Japan*, 1972, **45**, 770.

[5] C. G. Dodd and S. Ray, *Clays and Clay Minerals*, 1960, **8**, 237.

that the yellow colouration is due to the presence of a dipositive radical cation of benzidine (bzn^{2+}). This species is thought to be formed by a disproportionation reaction caused by production of protons at the clay surface as the clay is dehydrated. Protonated benzidine species ($Hbzn^{+}$) are also thought to be produced [equation (1)].

$$2bzn^{+} + H^{+} \rightleftharpoons bzn^{2+} + Hbzn^{+} \qquad (1)$$

The surfaces of dehydrated montmorillonite are known to be acidic, the protons arising from ionisation of structural OH^{-} groups or residual water molecules.[6] Evidence that amine molecules, such as pyridine for example, present at the clay surfaces may be protonated has previously been given.[7] The suggestion that protons are involved in the blue to yellow transformation of benzidine–montmorillonite is therefore not unreasonable. In view of the contrasting interactions of benzidine, *NNN'N'*-tetramethylbenzidine, and *trans*-4,4'-diaminostilbene with montmorillonite, the conflicting literature on the benzidine system, and the lack of information on the other two, we considered further study worthwhile. Moreover we have reported [3] that it is possible to prepare both pre- and post-intercalation benzidine–montmorillonite complexes and this factor has not been recognised in previous studies. In the present study we report u.v. and visible reflectance and i.r. studies of the blue and yellow benzidine–montmorillonite complex and compare these with the spectra of solid derivatives of the radical species. We have also made a similar study of the *NNN'N'*-tetramethylbenzidine (tbzn)–and *trans*-4,4'-diaminostilbene (dsn)–montmorillonite complexes.

EXPERIMENTAL

The purification and preparative procedures used to prepare montmorillonite–benzidine and related complexes have been described elsewhere.[3] The perchlorate derivatives of the radical cations of the amines were prepared by literature methods.[8,9] The samples were characterised by the following analytical data for % $[ClO_4]^-$ (calculated values are given in parentheses): $[bzn][ClO_4]$, 34.2 (35.1); $[bzn][ClO_4]_2$, 50.1 (52.0); $[tbzn][ClO_4]$, 30.2(29.3); $[tbzn][ClO_4]_2$, 45.8 (45.3); and $[dsn][ClO_4]_2$, 45.3 (48.7).

Diffuse-reflectance spectra of powdered samples were recorded using a Unicam SP 1800 spectrophotometer. Spectra were plotted as the Kubelka–Monk function $f(R) = (1 - R^2)/2R$ where R is the reflectance of the sample at a given wavelength relative to a MgO standard. I.r. spectra of the clay samples were recorded using a Digilab Fourier-transform spectrometer. About 400 scans were used in the data-reduction process. Samples were ground with KBr and pressed to thin pellets which were mounted in a cell capable of evacuation to *ca.* 10^{-3} Torr.*

Mild dehydration of the organic–clay complexes was achieved in a vacuum desiccator over $CaCl_2$ and rigorous dehydration by heating the materials to *ca.* 375 K *in vacuo* at *ca.* 10^{-3} Torr. *X*-Ray diffraction measurements (made using a Phillips PW1050 diffractometer and filtered Cu-K_α radiation) indicated that montmorillonite following mild dehydration retained ' one layer ' of water as the *c* spacing was 12.3 ± 0.3 Å.[10] Rigorous dehydration results in removal of this residual water and the layer spacing collapses to 9.8 Å.[10] Unfortunately the necessarily *in situ c*-spacing measurements of the amine-intercalated clays could not be made but the behaviour of the montmorillonite and the data described in this work suggest that water molecules coexist with amine molecules following mild dehydration and that most or all of this water is removed on rigorous dehydration.

RESULTS

Benzidine–Montmorillonite.—(i) *Diffuse-reflectance studies.* Figure 1(*a*) is the diffuse-reflectance spectrum of the blue pre-intercalation benzidine complex and Figure 1(*b*) that of the same material following mild dehydration. Figure 1(*c*) and (*d*) are the reflectance spectra of the perchlorate derivatives of the uni- and di-positive benzidine radical cations (bzn^{+} and bzn^{2+}). It can be seen that the strong maxima at 600 and 400 nm (Table) observed for the blue benzidine–montmorillonite are closely paralleled by similar absorptions of the perchlorate salt of the bzn^{+}. On dehydration these bands decreased in intensity and a new band at 450 nm appeared [Figure 1(*b*)].

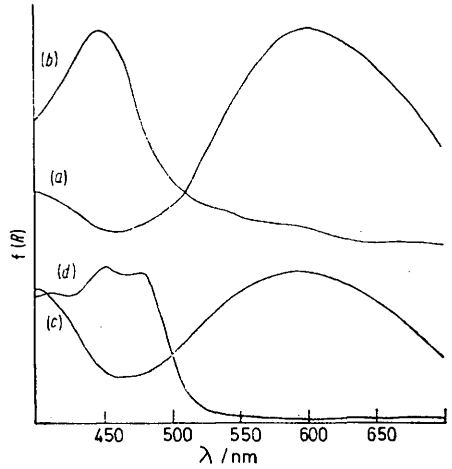

FIGURE 1 Diffuse-reflectance spectra of (*a*) the blue pre-intercalation benzidine complex; (*b*) the same material following mild dehydration; (*c*) $[bzn][ClO_4]$, and (*d*) $[bzn][ClO_4]_2$

The diperchlorate $[bzn][ClO_4]_2$ has a similar yellow colouration to the dehydrated benzidine–montmorillonite complex and its reflectance spectrum [Figure 1(*d*)] consisted of a structured peak centred at *ca.* 450 nm. It seems reasonable to associate the band at 450 nm of the dehydrated benzidine–montmorillonite with the presence of bzn^{2+} species. The loss of the ' fine ' structure in the spectrum of the clay complex is perhaps not unexpected due to the reduction in symmetry of the environment of the benzidine moiety in going from the crystalline perchlorate derivative to the clay complex. Post-intercalation complexes behaved in a similar fashion but it was not possible to produce a complete loss of the bands at 600 and 400 nm on mild

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* 1 Torr = (101 325/760) Pa.

[6] J. Fripiat, *Proc. 8th Internat. Congress Soil Sci.*, Bucharest, 1964, **1**, 171.

[7] V. C. Farmer and M. M. Mortland, *J. Chem. Soc.* (*A*), **1966**, 344.

[8] S. Hunig and W. Daun, *Chem. Ber.*, 1955, **88**, 1238.

[9] H. Wieland, *Chem. Ber.*, 1913, **46**, 3296.

[10] R. E. Grim, *Clay Mineralogy*, McGraw-Hill, New York, 1968.

dehydration. A complete change to the yellow material could, however, be brought about by addition of dilute (2M) HC to the blue post-intercalation benzidine complex. More surprisingly, addition of stronger acid caused complete loss of colour leaving a white complex.

Absorption maxima (nm) of the u.v. and visible-reflectance spectra of the montmorillonite–organic complexes and the perchlorate derivatives of the radical cations

Benzidine–montmorillonite				
Pre-intercalation complex (wet)	600			400
(dry)		450		
Post-intercalation complex (wet)	600	450		400
(dry)	600	450		400
[bzn][ClO$_4$]	600			400
[bzn][ClO$_4$]$_2$		450	490	
NNN′N′-Tetramethylbenzidine–montmorillonite				
Pre-intercalation complex (wet)	650		490	
(dry)	650		490	
Post-intercalation complex (wet)	650		490	
(dry)	650		490	
[tbzn][ClO$_4$]	650		490	
[tbzn][ClO$_4$]$_2$		545		380
trans-4,4′-Diaminostilbene–montmorillonite				
Pre-intercalation complex (wet)	640			
(dry)		450		
Post-intercalation complex (wet)		450		
(dry)		450		
[dsn]$^+$ (soln. spectrum)	630			
[dsn][ClO$_4$]$_2$		450		

(ii) *I.r. studies.* I.r. spectra of montmorillonite dried in air and rigorously dehydrated at 350 K at *ca.* 10^{-3} Torr are shown in Figure 2(*a*) and (*b*). The spectra are in good agreement with previous work.[11] The strong absorptions in the region 3 700—3 000 and 1 650 cm^{-1} are ascribed [11] to sorbed water and structural hydroxyl groups and those at 1 500—700 cm^{-1} of the dry clay to vibrations of the aluminosilicate framework. The bands at 2 965, 2 930, and 2 850 cm^{-1} are attributable to symmetrical and asymmetrical stretching frequencies of CH$_3$ and CH$_2$ groups and arise due to the presence of hydrocarbon contaminants (probably pump oil) at the clay surface.

The i.r. spectrum of the air-dried benzidine post-intercalation complex of montmorillonite, containing on the basis of u.v. and visible spectra bzn$^+$ and bzn^{2+}, showed several new bands and of these the band at 1 550 cm^{-1} was reversibly lost on further dehydration [Figure 3(*a*) and (*b*)]. Further absorptions at 3 410—3 420, 3 335, 2 600, and 2 585 cm^{-1}, present but not distinct in the air-dried sample, became evident on rigorous dehydration of the complex. I.r. spectra of benzidine, benzidine hydrochloride, and benzidine mono- and di-perchlorates revealed that only the radical salts absorb at 1 550 cm^{-1}. This band is assigned to a vibrational mode involving the –C–N$^+$– linkage of the radicals as its frequency is intermediate between those of the bands at 1 680 and 1 230—1 030 cm^{-1} observed [12] for the –C–N– and –C=N– bonds respectively. Thus further evidence is provided for the presence of radical species at the clay surfaces. The absorptions at 2 600 and 2 580 cm^{-1}, seen indistinctly in the air-dried material and more sharply so in the rigorously dehydrated material and also observed for benzidine dihydrochloride, can be assigned to combinations and overtones of NH$_3^+$ groups.

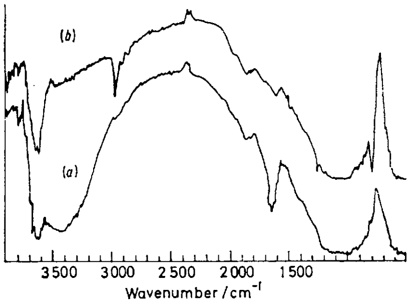

FIGURE 2 I.r. spectra of (*a*) air-dried montmorillonite; and (*b*) rigorously dehydrated montmorillonite

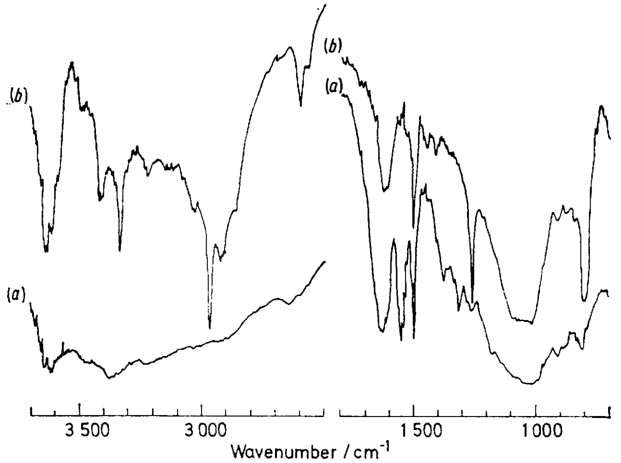

FIGURE 3 I.r. spectra of (*a*) post-intercalation benzidine–montmorillonite; and (*b*) this material following further dehydration (note change of scale)

NNN′N′-*Tetramethylbenzidine–Montmorillonite.*—(i) *Diffuse-reflectance studies.* The absorption maxima of the green tbzn–montmorillonite complex occur at 650 and 490 nm (Table) and these closely correspond to maxima in the spectrum of the perchlorate salt of tbzn$^+$. Mild dehydration of clay produced no significant change in the spectrum. No peak at 380 nm corresponding to tbzn^{2+} was observed. However, rigorous dehydration of the tbzn–clay complexes resulted in reversible loss of colour. This change could also be brought about by acidification and in this respect the tbzn system is analogous to the benzidine system.

(ii) *I.r. studies.* A number of new bands not seen in the spectrum of montmorillonite appeared in the spectra of the tbzn–clay complexes. The green air-dried samples showed absorptions at 1 550 and 1 540 cm^{-1} which disappeared, reversibly, on rigorous dehydration. A doublet at 1 410 and 1 400 cm^{-1} was also seen in the spectrum of the air-dried sample and on rigorous dehydration the intensity of this band decreased considerably. Comparison of the spectra of tbzn and the perchlorate salts of tbzn$^+$ and tbzn^{2+} reveals that tbzn shows no absorption at 1 550 cm^{-1}, tbzn$^+$ absorbs at 1 550 cm^{-1}, and tbzn^{2+} absorbs at 1 575 cm^{-1}. The observation of a band at 1 550 cm^{-1} in the air-dried sample, therefore, is compatible with the presence of tbzn$^+$ at the clay surfaces. The spectrum of the rigorously dehydrated

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[11] V. C. Farmer and J. D. Russel, *Spectrochim. Acta*, 1964, **20**, 1149.

[12] K. Nakamoto, 'Infra-red Absorption Spectroscopy,' Holden-Day Inc., San Francisco and Nankodao Co., Ltd., 1962.

tbzn–clay exhibited a broad band at 2 400—2 750 cm^{-1}. This is attributable [9] to the N–H$^+$ stretching frequency, together with combinations and overtones of protonated tertiary amino-groups. Protonated tbzn moieties can therefore exist at the clay surfaces. The absorptions at 1 400 and 1 410 cm^{-1} seen in the air-dried clay complex but decreasing on dehydration are assigned to the symmetrical stretching mode of methyl groups. This band normally appears at 1 380 cm^{-1} but is known [12] to shift to higher frequency when the CH_3 group is adjacent to an electron-withdrawing constituent such as the positively charged nitrogen atom in tbzn$^+$. Protonated tbzn species are not expected to absorb in this region and thus the observed decrease in intensity of the doublet on dehydration is expected.

trans-4,4′-*Diaminostilbene–Montmorillonite*.—(i) *General*. Treatment of aqueous suspensions of montmorillonite with aqueous solutions of 4,4′-diaminostilbene (dsn) results in a green product which on dehydration changes to brown, the process being reversed by rehydration.[13] *X*-Ray powder-diffraction photographs demonstrated no change in the *c* spacing of the montmorillonite and therefore it is considered that this complex is analogous to the preintercalation benzidine–clay complex. It was not possible to prepare a flocculated post-intercalation complex because of the low solubility of dsn in water. However, a green flocculated intercalate of dsn in montmorillonite (*c* 14.5 Å) was prepared by use of the more soluble dsn dihydrochloride. This green product rapidly turns brown in air and the green colour cannot be restored by rehydration. However, addition of base produces the green colour and on acidification the brown material returns. Potentiometric titrations established that 70 milliequivalents of dsn·2HCl reacted with 100 g of clay, therefore indicating that dsn is initially taken up as H_2dsn^{2+}.

(ii) *Diffuse-reflectance spectra*. The diffuse-reflectance spectra of the green and brown materials, irrespective of the method of preparation, showed maxima at 640 and 450 nm respectively. The solid perchlorate salt of dsn^{2+} has a maxima at 450 nm. Solid derivatives of dsn$^+$ could not be prepared but it was possible to record a solution spectrum of the transient green colour produced on addition of iodate to an aqueous solution of dsn·2HCl. This solution absorbed at 630 nm and it is reasonable to ascribe the green and brown colourations to the presence of dsn$^+$ and dsn^{2+} at the clay surfaces. It is of interest to note that dsn$^+$ may be stabilised at the clay surfaces.

DISCUSSION

The previous conclusion,[2] that the blue colour of benzidine–montmorillonite is associated with the presence of monoradical cations of benzidine at the clay surfaces, is confirmed in this work on the basis of u.v. and visible reflectance and i.r. transmission data. Our work, together with that of Matsunaga,[4] strongly suggests that the earlier conclusion, that the yellow colouration is due to protonated monoradical cations of benzidine, should be discarded and that the colouration is due to the presence of bzn^{2+} at the clay surfaces. This implies, therefore, that the disproportionation mechanism of Matsunaga is operative at the clay surfaces. Further evidence for the disproportionation mechanism is provided by the i.r. spectra which indicate that protonated benzidine moieties exist at the surfaces of the mildly dehydrated clay. The view that protons, which are known [6] to be produced at dehydrated clay surfaces, are involved in the reaction is supported as the blue to yellow transformation can also be brought about by external changes in pH. After rigorous dehydration of the benzidine–montmorillonite complex there is no evidence for the presence of benzidine radicals and it would appear that under conditions of high acidity only colourless protonated benzidine moieties are present. It should be noted, however, that a fraction of the total benzidine sorbed at the clay surface is oxidised by substitutional iron(III).[14] To explain the observed change of iron(II), so produced, back to iron(III) on dehydration it was necessary to invoke a second equilibrium which led to the production of Hbzn$^+$. It would appear, therefore, that the disproportionation mechanism of Matsunaga coexists with this reaction and involves the dominant fraction of benzidine moieties initially oxidised at Lewis-acid sites which do not themselves involve iron.

The green colour of the tbzn–montmorillonite complex is clearly due to the presence of tbzn$^+$. The absence of tbzn^{2+} after mild dehydration is in direct contrast to the situation that exists with benzidine. As the blue benzidine radicals are thought to interact in a pair-wise (or more than pair-wise) manner the electron-transfer process, inferred by the disproportionation mechanism, probably occurs between adjacent molecules. It is possible that this transfer mechanism in inhibited because the presence of the sterically bulky methyl groups may inhibit close approach of tbzn molecules. Alternatively, electron transfer may occur *via* a N–H bond. Indeed the stability of a single colour on clays is particularly associated with tertiary-amine complexes of the clay.[15] The disappearance of the green colour on rigorous dehydration is analogous to the benzidine system as only protonated tbzn moieties exist at the clay surfaces under these conditions.

The green-brown transition of the *trans*-4,4′-diaminostilbene pre-intercalation complex prepared from the neutral diamine is also compatible with the initial production of the green dsn$^+$ which yield brown dsn^{2+} on dehydration. These species are also responsible for the colouration of the material prepared from the dihydrochloride. It would appear that the diprotonated dsn species are oxidised at Lewis-acid sites at the clay surfaces (the excess of positive charge being balanced by an increase in the negative-layer charge of the clay) and that protons are released and take on the role of exchangeable cations. These protons produce an acidic environment even under ' wet ' conditions and under these conditions, if the Matsunaga mechanism operates, brown diradicals

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[13] D. T. B. Tennakoon, J. M. Thomas, M. J. Tricker, and S. H. Graham, *J.C.S. Chem. Comm.*, 1974, 124.

[14] D. T. B. Tennakoon, J. M. Thomas, and M. J. Tricker, *J.C.S. Dalton*, 1974, 2211.

[15] D. T. B. Tennakoon, J. M. Thomas, and M. J. Tricker, unpublished work.

are expected to be present. On addition of NaOH the protons are cation exchanged by Na^+ ions and green unipositive radicals are produced.*

In general, pre-intercalation complexes undergo colour changes more easily than the post-intercalation complexes. The implication is that the exterior surfaces of the organic–clay complexes are more readily dehydrated than the interior. Protons are therefore produced more readily by dehydration at the exterior surfaces than at the interior. Thus the colour changes are more facile at the exterior surfaces. However, the possibility that the dehydrated interior surfaces are inherently less acidic than the exterior cannot be discounted.

The reactions described in this paper involve both Lewis- and Brønsted-acid sites at the clay surfaces. It should be possible, therefore, by making a more quantitative study involving the use of these and similar amines of known basic strength and ionisation potential, to reveal further information about the nature of these sites and hence the catalytic properties of clay minerals.

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* It should be noted that further H_2dsn^{2+} species can be introduced into the clay at this stage by cation exchange.