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# The intercalation of 2,2′-bipyridine and 1,10-phenanthroline and their complexes with iron within the interlayer regions of montmorillonite clay

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## Abstract

The intercalation of 2,2′-bipyridine and 1,10-phenanthroline and their complexes with iron within the interlayer regions of montmorillonite clay has been examined by a range of techniques. The intercalation of 2,2′-bipyridine within different size fractions of natural- and sodium-exchanged montmorillonite has been shown by X-ray diffraction to increase the interlayer spacings. Infrared spectroscopy indicates that some of the intercalated 2,2′-bipyridine undergoes complex formation with $Fe^{2+}$ located at the surface structure of the interlayer region. The intercalation into montmorillonite of $Fe(bipy)_3{}^{2+}$ and $Fe(phen)_3{}^{2+}$ complexes from solution has been monitored by recording the visible absorbance spectra of the supernatant liquids withdrawn from the preparation media. The extent of intercalation has been correlated with the cation exchange capacity of the clay and the different behaviour of the two complexes is associated with their diffusion into the interlayer regions of the montmorillonite clay.

## Introduction

Montmorillonite is an expanding layer silicate mineral and consists of sheets of aluminium ions in octahedral oxygen/hydroxyl coordination sandwiched between two tetrahedral silica sheets [1, 2]. The aluminium cations can be randomly substituted by cations of similar size such as $Mg^{2+}$ and, albeit to a lesser extent, $Fe^{3+}$ and $Fe^{2+}$. The resulting charge deficit is distributed over the surfaces of the 2:1 layer units and is compensated by the adsorption of hydrated cations which cause the layer units to stack on top of each other. The spaces between the layer are known as the interlayer regions and the cations which are accommodated within such layers are called interlayer and are exchangeable. Neutral polar and cationic organic molecules can intercalate between the expanding layers of clay minerals. The mechanism of intercalation of the neutral polar molecules involves coordination to the resident charge-neutralising inorganic cations such that organocations are formed which displace the inorganic cations and are held by Coulombic attraction to the clay surface [3]. These types of interlayer adsorptions into montmorillonite clay involving 2,2′-bipyridine and 1,10-phenanthroline and their respective salts have already been the subject of several investigations [4–7].

We have reported [8] on our studies by $^{57}Fe$ Mössbauer spectroscopy of size fractionated and iron-exchanged montmorillonite clays and we now report on our investigations of the intercalation of 2,2′-bipyridine and 1,10-phenanthroline between the layers of montmorillonite to examine the changes in the interlayer spacing and the location of the intercalated species. We also report on the intercalation of the complexes $Fe(bipy)_3{}^{2+}$ and $Fe(phen)_3{}^{2+}$, where bipy is 2,2′-bipyridine and phen is 1,10-phenanthroline, within montmorillonite clay and the factors which influence the extent of intercalation.

## Experimental

The Clay Minerals Society ‘source clays’ STx-1 and SWy-1 containing 0.56 and 2.60% iron, respectively, and which were sometimes sodium exchanged, were size fractionated by methods described previously [8].

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Reactions of the clays with 2,2′-bipyridine were performed by adding aliquots (10 $dm^3$) of 2,2′-bipyridine in either ethanol or 1:10 ethanol:water solution to 0.2 g quantities of the different size fractions of natural- and sodium-exchanged montmorillonite. The products were isolated by either filtration or centrifugation and dried in air or by freeze-drying techniques.

The intercalation of the complexes $Fe(bipy)_3{}^{2+}$ and $Fe(phen)_3{}^{2+}$, where bipy is 2,2′-bipyridine and phen is 1,10-phenanthroline, within size-fractionated sodium-exchanged SWy-1 montmorillonite was performed under nitrogen at pH 1.8. Aliquots containing $3 \times 10^{-4}$ mol of either 2,2′-bipyridine or 1,10-phenanthroline in 1:10 ethanol:water solutions were added to suspensions of montmorillonite in solutions of iron(II) chloride in dilute hydrochloric acid (100, 80, 60, 40, 20 mmol of $Fe^{2+}$ per 100 $g^{-1}$ of clay). The suspensions were diluted with water, shaken (30 min), and allowed to stand. Samples of the supernatant liquids were withdrawn for examination by visible absorbance spectroscopy and the remaining suspensions centrifuged. The sediments were isolated, washed with water, and freeze-dried.

Silica gel (60–120 mesh), which had been washed with dilute sodium hydroxide solution (0.1 M) to remove superficial silicic acid and dried at 100 °C (1 h), was also treated with aqueous iron(II) chloride and either 2,2′-bipyridine or 1,10-phenanthroline by analogous methods.

Sodium-exchanged SWy-1 montmorillonite was also treated with an aqueous solution containing iron(III) nitrate and 2,2′-bipyridine by similar methods.

Powder X-ray diffraction patterns were recorded with a Picker powder X-ray diffractometer operating under a Philips PW 1710 control system using Cu $K\alpha_1$ radiation. Step-scan powder X-ray diffraction patterns were recorded in the range 2° of $2\theta$ to 12° of $2\theta$ at 0.05° per 20 s.

$^{57}Fe$ Mössbauer spectra were recorded at 298 and 77 K from samples containing less than 50 mg iron $cm^{-2}$ using a microprocessor controlled Mössbauer spectrometer with a 25 mCi $^{57}Co/Rh$ source at 298 K. The spectra were computer fitted and the chemical isomer shift data quoted relative to metallic iron.

Infrared spectra were recorded from samples prepared as KBr discs with a Pye Unicam SP3-100 infrared spectrophotometer.

Visible absorbance spectra were recorded with a Shimadzu UV-240 spectrophotometer. Measurements were made at 522 nm for the 2,2′-bipyridine systems and at 510 nm for the 1,10-phenanthroline preparations using dilute solutions of 2,2′-bipyridine or 1,10-phenanthroline as standards.

## Results and discussion

### *Montmorillonite treated with 2,2′-bipyridine*

Treatment of 0.5–1 and $<2$ $\mu m$ size fractions of natural- and sodium-exchanged STx-1 and SWy-1 montmorillonite with 2,2′-bipyridine gave products in which the intensity of the pale pink colour increased in the smaller size clay fractions and also in the high-iron content SWy-1 montmorillonite materials.

The step-scan powder X-ray diffraction pattern recorded from the freshly prepared $<2$ $\mu m$ fraction of the sodium-exchanged SWy-1 montmorillonite showed a poorly-resolved peak at $d = 12.44$ Å which was replaced in the pattern recorded from the material heated at 110 °C by a well resolved peak at $d = 9.44$ Å. The results endorse observations reported previously [9] and suggest that the exchangeable-sodium ions are hydrated in the freshly prepared material but are at least partially dehydrated at moderate temperatures to give materials in which the interlayer region is of more uniform size. Indeed the peak at *c.* 9.5 Å has been associated [9] with the complete absence of interlayer water.

Treatment of this montmorillonite with 15, 50, 150, 300 and 750 mmol of 2,2′-bipyridine per 100 g of clay produced materials which gave powder X-ray diffraction patterns which were characterised by an increasingly well-resolved peak corresponding to an interlayer spacing of 18.39 Å for the 750 mmol preparation. This value is similar to that reported previously [10] for montmorillonite when treated in a similar manner. The data are consistent with the intercalation of 2,2′-bipyridine within the interlayer regions of montmorillonite clay.

We contend that the pink colour which is observed when 2,2′-bipyridine is added to montmorillonite is significant and is indicative of the interaction between the compound and $Fe^{2+}$ [10]. This colour has been observed for the interaction of 2,2′-bipyridinium dihydrobromide with $Na^+$-montmorillonite and has been considered to result from the complexation of the 2,2′-bipyridinium species with the $Fe^{2+}$ associated with oxides at the clay surface and/or to coordination to $Fe^{2+}$ at the broken edges of the clay lattice structure [3, 4]. This interpretation is supported by the red colour of the low-spin $Fe(bipy)_3{}^{2+}$ complex which can be formed from the direct combination of $Fe^{2+}$ ions and 2,2′-bipyridine in aqueous or ethanolic solutions [11, 12]. $Fe^{3+}$ ions are known to react with 2,2′-bipyridine to give brown binuclear complexes of the type $[(Fe(bipy)_2)_2O]^{4+}$ [13].

The infrared data recorded from 2,2′-bipyridine, $Fe(bipy)_3Cl_2$ supported on silica, $[(Fe(bipy)_2)_2O][(NO_3)_2]$ supported on silica, and $Na^+$-montmorillonite following treatment with 750 mmol of 2,2′-bipyridine per 100 $g^{-1}$ of clay are recorded in Table 1. The infrared data recorded from 2 $\mu$m sodium-exchanged SWy-1 montmorillonite are summarised in Table 2.

The infrared spectrum recorded from montmorillonite when treated with 2,2′-bipyridine showed absorption bands, e.g. at 760 $cm^{-1}$, which could be associated with 2,2′-bipyridine, together with other peaks which were not attributable to either 2,2′-bipyridine or montmorillonite. The infrared spectrum recorded from silica-supported $Fe(bipy)_3Cl_2$ showed absorption bands at 780, 800 and at *c.* 1440, 1465 and 1600 $cm^{-1}$ which coincide with similar absorption bands recorded from the 2,2′-bipyridine-treated clay. The spectrum from silica supported $[(Fe(bipy)_2)_2O][(NO_3)_2]$ was significantly different from all the other spectra. Hence the infrared data suggest that the interlayer spaces of the montmorillonite are occupied by the $Fe(bipy)_3{}^{2+}$ complex together with some unreacted bipyridine.

Although $^{57}$Fe Mössbauer spectroscopy was unable to detect the presence of $Fe^{2+}$ in any of the materials examined, it must be acknowledged that the number of $Fe^{2+}$ species necessary for complex formation, and hence the pink colour, could easily be below the limit of detection by Mössbauer spectroscopy. Hence the location of the $Fe^{2+}$ species which give rise to complex formation is difficult to define with precision.

It would seem unlikely that the $Fe^{2+}$ species are present as impurity phases bound to the montmorillonite clay since such species would undergo facile aerobic oxidation to $Fe^{3+}$ and give rise to brown complexes of the type $[(Fe(bipy)_2)_2O]^{4+}$. Similarly, any unbound $Fe^{2+}$-containing oxide within the interlayer region would also be expected to undergo oxidation. In these respects it is pertinent to note that the washings obtained by shaking the intercalates with ethanol were shown by visible spectrophotometry to be free of any $Fe(bipy)_3{}^{2+}$ species which, if derived directly from unbound $Fe^{2+}$ species, would dissolve in ethanol and absorb at 522 nm [4, 15]. Previous work [4] has shown that the coloured complex is slowly removed from between the layers by the addition of excess cetylpyridinium bromide. The process involves the adsorption of the cetylpyridinium species, an expansion of the interlayer region, and the replacement of the charged $Fe(bipy)_3{}^{2+}$ complex by the cetylpyridinium cation. The coordination of 2,2′-bipyridine to $Fe^{2+}$ which is isomorphously substituted for aluminium in the octahedral or tetrahedral sheets is unlikely except in situations where the $Fe^{2+}$ is exposed at broken edges. Hence, a model for the occurrence of the pink colour in 2,2′-bipyridine-treated montmorillonite and achieved via the formation of a relatively immobile $Fe(bipy)_3{}^{2+}$ complex would need to involve the location of $Fe^{2+}$ species in reasonably accessible sites. It would seem likely therefore that the 2,2′-bipyridine which is intercalated as a neutral species within the SWy-1 montmorillonite interlayer regions is coordinated to $Fe^{2+}$ species located at the clay surface. The observed

TABLE 1. Infrared absorptions ($cm^{-1}$) recorded in the regions 1600–1300 and 800–700 $cm^{-1}$ from 2,2′-bipyridine and its products with iron(II), iron(III) and montmorillonite[a]

| 2,2′-Bipyridine | $Fe(bipy)_3Cl_2$ supported on silica | $[(Fe(bipy)_2)_2O][(NO_3)_2]$ supported on silica | $Na^+$-montmorillonite intercalated with 750 mmol 2,2′-bipyridine per 100 g of clay |
|---|---|---|---|
| | 1600m | | 1595m |
| 1580s | | 1582m | |
| 1557m | | | |
| | | 1524m | |
| 1500w | | | |
| | | | 1480m |
| | 1465m | | 1470m |
| 1450s | | | |
| | 1440m | 1440m | 1438m |
| | | | 1422sh |
| 1412s | | | |
| | | 1380vs | |
| | 1310w | | 1310vw |
| | 800sh | | 800m |
| | 780vs | | 780sh |
| 758vs | | | 760vs |
| | 730vs | 734vs | |

[a] vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

TABLE 2. Infrared absorptions recorded from <2 μm sodium-exchanged SWy-1 montmorillonite

| Frequency of absorption ($cm^{-1}$) | Assignment (ref. 14) |
|---|---|
| 3650sh | (Mg,Al) – OH str |
| 3640s | (Al,Al) – OH str |
| 3435m | loosely adsorbed water O–H str |
| 3240sh | crystal water H–O–H str |
| 1615m | loosely adsorbed water O–H bend |
| 1115sh | Si–O str |
| 1090sh | Si–O str |
| 1040s | Si–O–Si str |
| 1020s | Si–O–Si str |
| 915m | (Al,Al) – OH bend |
| 882w | (Al,Fe) – OH bend |
| 835w | (Al,Mg) – OH bend |
| 828sh | (Al,Mg) – OH bend |
| 800w | (Al,Mg) – OH bend |
| 623w | Al–O str |

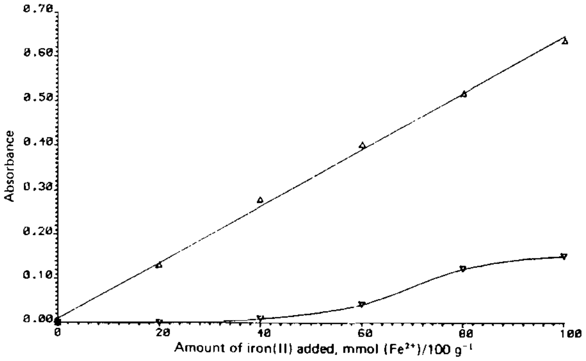

Fig. 1. Plot of absorbance of supernatant liquids withdrawn from $Fe(bipy)_3{}^{2+}$ treatments of silica gel (△) and sodium-exchanged SWy-1 montmorillonite (▽) against the initial concentrations of $Fe^{2+}$.

increase in intensity of colour with clay particles of smaller size is indicative of the binding of the ligand to $Fe^{2+}$ at the broken edges of the clay lattice.

### *Intercalation of $Fe(bipy)_3{}^{2+}$ and $Fe(phen)_3{}^{2+}$ complexes within montmorillonite*

The intercalates of the $Fe(bipy)_3{}^{2+}$ and $Fe(phen)_3{}^{2+}$ complexes with <2 μm SWy-1 sodium-exchanged montmorillonite clays are best considered by comparison with the complexes supported on silica which were formed by analogous methods.

The supernatant liquid withdrawn from the silica-$Fe(bipy)_3{}^{2+}$ and -$Fe(phen)_3{}^{2+}$ preparation media were examined by visible absorbance spectroscopy. Plots of the absorbance against the initial $Fe^{2+}$ concentration in the preparation media gave straight lines (Figs. 1 and 2). Linear regression enabled the calculation of the correlation coefficients for $Fe(bipy)_3{}^{2+}$ and $Fe(phen)_3{}^{2+}$ as 0.998903 and 0.999165, respectively. Line equations of $y=0.0063343x+0.00995$ and $y=0.0043714x+0.00410$ were evaluated which, for a given absorbance, permitted the calculation of the concentration of $Fe(bipy)_3{}^{2+}$ or $Fe(phen)_3{}^{2+}$ remaining in solution. Isotherms for the adsorption of 1,10-phenanthroline by a range of clays, including a $Na^+$-montmorillonite, oxides and silica gel are recorded in the literature [7].

Given that the bipyridine and phenanthroline compounds were added to the montmorillonite under acidic conditions, it would be reasonable to expect the neutral molecules to be protonated to give the respective organocations. It could be envisaged that 2,2′-bipyridine would be released from the bipyridinium dichloride according to the equilibrium

$$\text{2,2}'\text{-bipyridinium}^{2+} + 2Cl^- \rightleftharpoons \text{2,2}'\text{-bipyridine} + 2H^+ + 2Cl^-$$

and that the released bipyridine would give rise to the formation of the tris complex and an expansion of the interlayer region. Earlier work [4] has shown that the isotherms for the adsorption of the bipyridinium organocations are of the high affinity or H-type [16]. In the work reported here the plots of visible absorbance against the initial $Fe^{2+}$ concentration in the supernatant liquids withdrawn from the preparation media of the montmorillonite intercalation reactions with $Fe(bipy)_3{}^{2+}$ and $Fe(phen)_3{}^{2+}$ were sigmoid (Figs. 1 and 2) indicating that all of the complex which was formed was also adsorbed by the clay at low concentrations. This is also evident in the isotherms for adsorption of 1,10-phenanthroline by $Na^+$-montmorillonite [7]. Given that 76.4 mmol(+) 100 $g^{-1}$ of clay corresponds to the maximum cation exchange capacity of the SWy-1 montmorillonite [17], the plots demonstrate the

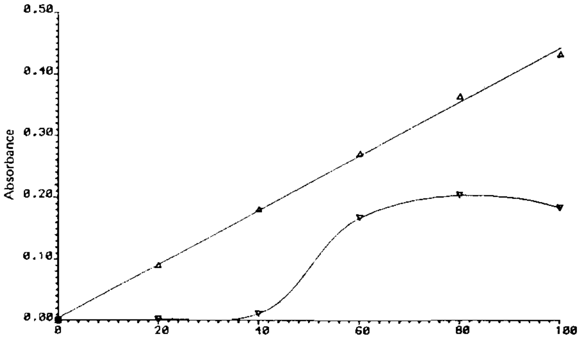

Fig. 2. Plot of absorbance of supernatant liquids withdrawn from $Fe(phen)_3{}^{2+}$ treatments of silica gel (△) and sodium-exchanged SWy-1 montmorillonite (▽) against the initial concentrations of $Fe^{2+}$.

limitations on the uptake of the $Fe^{2+}$ by the clay at high $Fe^{2+}$ concentrations in solution.

The extent of the association of the complexes with the clay is expressed in terms of the cation exchange capacity of the clay as is shown in Fig. 3. In the case of 2,2'-bipyridine the data showed that when 100 mmol of $Fe^{2+}$ were added per 100 $g^{-1}$ of clay only 22.3 mmol(+) of $Fe^{2+}$ was left in solution. The amount associated with the clay (77.7 mmol(+) 100 $g^{-1}$) is similar to the cation exchange capacity of the clay [17]. The result suggests that the measurement of $Fe(bipy)_3{}^{2+}$ concentrations in solution can provide a facile method for measuring the cation exchange capacities of clays by adding known amounts of $Fe^{2+}$ and 2,2'-bipyridine to a $Na^+$-exchanged clay and estimating the uptake of the $Fe(bipy)_3{}^{2+}$ complex for different $Fe^{2+}$ concentrations. For 1,10-phenanthroline the maximum absorbance was consistent with a concentration of 46.6 mmol(+) 100 $g^{-1}$ of the $Fe(phen)_3{}^{2+}$ complex in solution. When 100 mmol of $Fe(phen)_3{}^{2+}$ complex per 100 $g^{-1}$ of clay was added only 40.7 mmol(+) of the complex was detected in solution and the remaining 59.3 mmol was presumed to be associated with the clay. Increased adsorptions would be expected in less acidic conditions because previous work [7] has shown that 1,10-phenanthroline adsorption by $NH_4{}^+$-exchanged montmorillonite is maximised at pH values between pH 6 and 7 where 93 and 99% of the molecules are in the non-protonated form.

It is to be expected that the 1,10-phenanthroline will, like 2,2'-bipyridine, be largely in the protonated form under the acidic pH of the reaction medium and that an equilibrium will be established between the organocation species and any non-protonated phenanthroline. Since the $Fe^{2+}$ is added to the clay-containing medium before the addition of the ligand, some exchange between $Fe^{2+}$ and $Na^+$ within the interlayer region can reasonably be expected. Hence the non-protonated 1,10-phenanthroline will associate with $Fe^{2+}$ at the clay surface and give rise to an interlayer expansion. It can be envisaged that the expansion of the interlayer spacing allows the subsequent diffusion of fully formed tris complexes from the solution into the interlayer spaces.

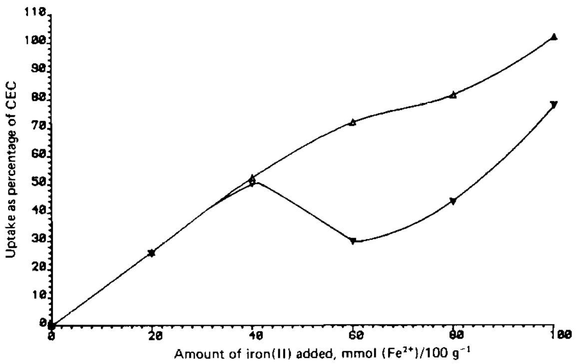

Fig. 3. Percentage uptake of $Fe(bipy)_3{}^{2+}$ (△) and $Fe(phen)_3{}^{2+}$ (▽) by sodium-exchanged SWy-1 montmorillonite with respect to the cation exchange capacity of the clay.

The uptake of the complexes from solution might reasonably be expected to be limited by both the diffusion of the species to and from the interlayer regions and the cation exchange capacity of the clay. Diffusion from the solution to sites in the interlayer region will be influenced by the sizes of the gaps between the layers and the numbers of adsorbate species between the layers. Under these circumstances the uptake of the $Fe^{2+}$ complexes from solution would be expected to decrease at higher complex concentrations, since steric hindrance would become significant and the uptake would then tend to a constant value as the cation exchange capacity is approached. The data are consistent with such a model for the intercalation of $Fe(bipy)_3{}^{2+}$. However, the $Fe(phen)_3{}^{2+}$ complex exhibits different behaviour suggesting that, although the phenanthroline complex initially occupies the exchange sites with ease, its bulky nature inhibits the diffusion of more $Fe(phen)_3{}^{2+}$ into the interlayer regions. However, the data also show that at the higher concentrations of the complex the 2:1 layer units are pushed apart and thereby give rise to an increased percentage uptake. The variation in percentage of the iron complexes with respect to the cation exchange capacity of the clay (Fig. 3) is consistent with this model in that the uptake of the $Fe(bipy)_3{}^{2+}$ complex increases linearly as a result of the facile occupation of the exchange sites by $Fe(bipy)_3{}^{2+}$. The data recorded from the $Fe(phen)_3{}^{2+}$ complex are also consistent with the model since they reveal an initial easy diffusion of $Fe(phen)_3{}^{2+}$ complexes in the exchange sites between the layers followed by a sharp decrease and then an increase in the uptake of the complex as the 2:1 layers are pushed further apart.

The $^{57}Fe$ Mössbauer spectra recorded from the dried silica-supported-$FeCl_2 \cdot 4H_2O$, -$Fe(bipy)_3{}^{2+}$ and -$Fe(phen)_3{}^{2+}$ complexes gave parameters which are collated in Table 3. The small chemical isomer shifts, $\delta$, and quadrupole splittings, $\Delta$, recorded from the silica-supported-$Fe(bipy)_3{}^{2+}$ and -$Fe(phen)_3{}^{2+}$ complexes are consistent with the presence of low-spin $Fe^{2+}$ (18, 19]. The $^{57}Fe$ Mössbauer spectra recorded at 77 K from the $Fe(phen)_3{}^{2+}$ and $Fe(bipy)_3{}^{2+}$ (Fig. 4) intercalated montmorillonites were each characterised by two partially superimposed quadrupole split absorptions (Table 3). One doublet, $\delta$ *c.* 0.40 mm $s^{-1}$, $\Delta$ *c.* 0.54 mm $s^{-1}$, was characteristic of

TABLE 3. $^{57}$Fe Mössbauer parameters recorded at 77 K from $FeCl_2 \cdot 4H_2O$, $Fe(bipy)_3^{2+}$ and $Fe(phen)_3^{2+}$ supported on silica and intercalated within sodium-exchanged SWy-1 montmorillonite

| Sample | $\delta \pm 0.01$ (mm $s^{-1}$) | $\Delta \pm 0.02$ (mm $s^{-1}$) |
|---|---|---|
| $FeCl_2 \cdot 4H_2O$/silica | 0.66 | 0.65 |
| | 1.25 | 2.59 |
| $Fe(bipy)_3^{2+}$/silica | 0.38 | 0.33 |
| Sodium-exchanged SWy-1 montmorillonite | 0.46 | 0.54 |
| $Fe(phen)_3^{2+}$/silica | 0.39 | 0.27 |
| $Fe(bipy)_3^{2+}$/ | 0.38 | 0.34 |
| montmorillonite | 0.41 | 0.54 |
| $Fe(phen)_3^{2+}$/ | 0.38 | 0.28 |
| montmorillonite | 0.38 | 0.53 |

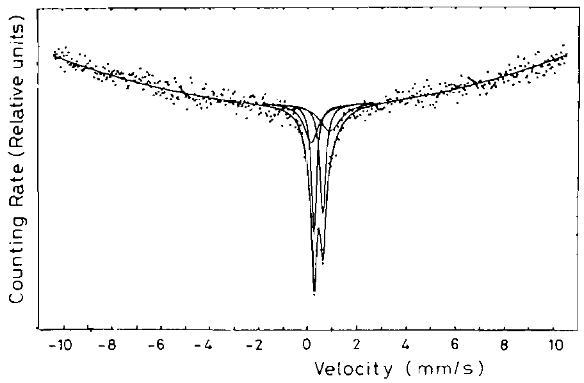

Fig. 4. $^{57}$Fe Mössbauer spectrum recorded at 77 K from sodium-exchanged montmorillonite intercalated with 80 mmol of $Fe(bipy)_3^{2+}$ per 100 $g^{-1}$ of clay.

high-spin $Fe^{3+}$ and can be associated with the iron within the montmorillonite lattice. The other doublet in each spectrum, $\delta$ *c.* 0.38 mm $s^{-1}$, $\Delta$ *c.* 0.31 mm $s^{-1}$, may be attributed to low-spin $Fe^{2+}$ in the complexes intercalated within the interlayer regions of the montmorillonite structure. It is clear from the intense and well resolved Mössbauer spectra that a significant fraction of the complexes are successfully intercalated within the montmorillonite.

## Conclusions

The intercalation of 2,2′-bipyridine within montmorillonite clay has been shown by X-ray diffraction to result in an increase in the interlayer spacings. Infrared spectroscopy shows that the pink colour which accompanies this process is associated with some of the intercalated 2,2′-bipyridine complexing with $Fe^{2+}$ located at the surface of the interlayer region.

The intercalation of $Fe(bipy)_3^{2+}$ and $Fe(phen)_3^{2+}$ complexes from solution into montmorillonite has been monitored by recording the visible absorption spectra of the supernatant liquids withdrawn from the preparation media. The extent of intercalation has been correlated with the cation exchange capacity of the clay and the different behaviour of the two complexes associated with their diffusion into the interlayer regions of the montmorillonite clay.

## Acknowledgment

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