ORGANOMETALLIC CATION-EXchanged PHYLOSILICATES: EXCHANGE WITH CATIONS DERIVED FROM (CH₃)₂SnCl₂

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ABSTRACT: Complexes formed between 0.034 M dimethylin dichloride solutions and Na-montmorillonite at pH 2.4 and 4.0 have been characterized using ¹¹⁶Sn Mössbauer spectroscopy, X-ray diffraction, infrared spectroscopy, thermogravimetric analysis and water sorption isotherms. The dominant exchange cation at pH 2.4 is Me₂Sn⁺ characterized by an isomer shift, δ, and quadrupole splitting, Δ values of 1.25 and 3.80 mm s⁻¹, respectively. The major exchange cation at pH 4.0 is the dimer, [Me₂Sn(OH)]₂⁺, (δ = 1.38, Δ = 3.34 mm s⁻¹) although the monomer, Me₂Sn(OH)⁺, (δ = 0.95, Δ = 3.29 mm s⁻¹) is also present. These complexes have basal spacings of 15.0 and 16.0 Å, respectively, which are stable up to 200°C. Mössbauer spectroscopy has shown that these ions are converted to SnO₂ via Me₂SnO upon thermal degradation. The temperature at which these oxides appear coincides with the collapse of the basal spacing. Both complexes display BET Type IV isotherms for the adsorption of water, following thermal pretreatment at 150°C, but the complex prepared at pH 4.0 has a lower sorption capacity. Both complexes, contrary to the normal behaviour of layer-silicates, have a definite pore volume and no further uptake occurs when this is filled.

In two recent reports, Petridis and co-workers (Simopoulos et al., 1988; Petridis et al., 1989) have studied the behaviour of cationic dimethyltin(IV) species exchanged on to a Wyoming montmorillonite, with a view to producing SnO₂ pillared clays upon firing. Their preparation method (0.08 mol dm⁻³ Me₂SnCl₂ at pH 5.5), chosen to generate the trimer [[(CH₃)₂Sn]₃(OH)_4]²⁺ and thus maximize the Sn-loading on the clay, produced intercalates with d-spacings of 16.6 Å which were stable up to 200°C in air.

In 1978 Coughlan et al. prepared and investigated the catalytic properties of several alkyltin exchanged zeolites. They reported that dibutyltin exchanged zeolite Y was more active for the dehydration of pentanol to pentene than the dimethyltin exchanged form and attributed this to the relative acidities of the aquo-diakyltin(IV) ions (Nevett & Tobias, 1963). Coughlan’s dimethyltin samples, prepared from dimethyltin dichloride solutions at pH 1.8 and 3.3, were conditioned at 450°C in flowing hydrogen for six hours and the tin was thus unlikely to remain methylated.

Thus, with the current interest in the utilization of various cation-exchanged clays as acid catalysts across a range of novel and industrially significant processes (Adams, 1987; Ballantine, 1986), a study of dimethyltin(IV)-exchanged clay suggested itself for several
reasons. Firstly, the maintenance of a basal spacing near 16 Å up to 200°C would facilitate ingress and exit of reactant and product molecules to and from the active site at reasonably elevated temperatures. Secondly, the protons generated from the hydrolysis of the dimethyltin species and/or their noted Lewis acidity would provide the catalytic site. Thirdly, the presence of the methyl groups on the tin, which are small enough to leave exposed basal surface, may result in an enhanced and potentially useful hydrophobicity of the interlamellar region. Furthermore, the increasing utilization of organotin compounds as agrochemicals, anti-fouling agents and stabilisers in polymers such as PVC has directed justifiable concern over their environmental degradation pathway. This study may help clarify the nature and residence time of these species in clay bearing soils.

One of the problems associated with the utilization of organotin species is their ready hydrolysis in aqueous solutions. Tobias and co-workers (Tobias et al., 1962; Nevett & Tobias, 1963; Tobias & Yasuda, 1974; Tobias, 1978) have devoted considerable attention to the pH dependence of the hydrolysis product of di- and trimethyltin. For the purpose of this study, in which close control of the interlayer cation was desired, the most pertinent results are those reproduced in Fig. 1 for a 0.01 mol dm⁻³ solution of dimethyltin dichloride (Tobias & Yasuda, 1964; Tobias, 1978). At pH 2.4, a considerable quantity of monomeric Me₂Sn²⁺ is present, whilst at pH 4.0 the predominant species in solution is the dimer [Me₂SnOH]²⁺, although significant quantities of Me₂SnOH⁺ and, to a lesser extent, Me₂Sn²⁺ are also present. In this study we complement and extend the work of Petridis and co-workers (1989) by concentrating on the characterization of the exchange complexes formed between montmorillonite and a dimethyltin dichloride solution at pH values of 2.4 and 4.0, using ¹¹⁹Sn Mössbauer spectroscopy, X-ray diffraction (XRD), infrared (IR) spectroscopy, thermogravimetric analysis and water uptake studies. Furthermore, we present preliminary results for the interaction of these samples with the bases pyridine, 2-methylpyridine, 2,6-dimethylpyridine and n-butylamine, all of which can provide useful

Fig. 1. pH dependence of the Me₂Sn(IV) species in aqueous solution at a concentration of 0.01 mol dm⁻³.
Dimethyltin cation-exchanged clays

information concerning the number and type of acid sites in cation-exchanged clays (Breen et al., 1987; Breen, 1991a,b).

EXPERIMENTAL

The parent clay used in this study was a Wyoming montmorillonite supplied by Volclay Ltd., Wallasey, Cheshire. The nominally <2 μm fraction was collected by sedimentation and converted to the Na-exchange form by immersion in 1·0 M NaCl overnight. The clay was then washed free of electrolyte, dried at room temperature, ground with a mortar and pestle and stored. Chemical analysis of this sample by standard literature methods (Bennet & Reed, 1971) produced results consistent with a structural formula of (Si3.9Al0.1)(Al1.33Fe0.08Mg0.59)O10(OH)2. The cation exchange capacity (CEC), determined by a flame photometric method, was 68±2 mEq/100 g clay.

When 2 g of the <2 μm Na+-montmorillonite dispersed in 80 cm³ of water and 0·74 g (5 CEC) of Me₂SnCl₂ dissolved in a further 20 cm³ of water were rapidly mixed together the resulting mixture exhibited a pH of 2·4. Figure 1 shows that at this pH the major species in solution is Me₂Sn²⁺. In order to produce the dimeric cation [Me₂SnOH]²⁺, the pH of the mixture was adjusted to an initial value of 3·5, prior to adding the clay, using NaOH. Then, if necessary, the final pH of the mixture was adjusted to 4·0. The mixtures prepared at both pHs were stirred continuously for several hours before concentrating the clay by centrifugation and then repeating the exchange procedure. Following this second exchange the clay was washed until the supernatant solution was free of excess chloride. The resulting dimethyltin(IV)-exchanged clay was air-dried prior to further use. Some brief comparative work was carried out using the clay produced at pH 2·4, but most of the work concentrated on the sample prepared at pH 4·0. Two further clays were produced for comparative purposes. In these samples the exchange procedure described above was duplicated but in the absence of dimethyltin dichloride. The desired pH was obtained using HCl and NaOH solutions of suitable molarity. These samples will be referred to as acid-treated clays prepared at pH 2·4 and 4·0, respectively. Analysis for tin was carried out on a solution prepared by fusing 0·2 g cation-exchanged clay with molten NaOH, then extracting the fused mass with hydrochloric acid and diluting to 150 cm³. The solution was analysed for tin using an IL 357 atomic absorption spectrophotometer using a nitrous oxide flame and a detection wavelength of 235·5 nm.

A Jeol JDS 8X diffractometer using Cu-Kα radiation at 40 kV and 30 mA was used to determine the basal spacing of samples presented as an oriented film on a glass slide. The thermal stability of the basal spacings was determined by heating clay-coated glass slides in a muffle furnace at the temperatures indicated for a period of 16 h. The samples were cooled in a dessicator and transferred to the diffractometer as quickly as possible to prevent rehydration. Control experiments indicated that when rehydration did occur, it was slow compared to the time taken to record the diffractogram.

Thermogravimetric analyses were recorded on a Mettler TG50 thermobalance, equipped with a TC10A processor, at a heating rate of 20°C min⁻¹ under a flow of dry nitrogen carrier gas of 30 cm³ min⁻¹ using samples (~7 mg) pre-ground to <75 μm. Organic base-saturated samples were transferred directly from the base vapour into the thermobalance and thermograms recorded as above.

Self-supporting films (~2 mg cm⁻²) for IR analysis were prepared by evaporation of an aqueous slurry on a polyethylene backing which was subsequently removed. These air-dried
(20°C, r.h. = 60%) films were exposed to reagent grade bases as described above. Spectra were recorded at room temperature and atmospheric pressure and then after one hour at 50, 100, 150, 200 and 250°C using an evacuable variable temperature cell with a maximum operating temperature of 250°C. The spectrometer used was a Perkin-Elmer 783 equipped with a PE3600 data station.

Finely powdered samples were used in the Mössbauer studies to minimize anomalous line asymmetries arising from preferred orientations. Separate portions of the air-dried sample were pretreated for 16 h at 120, 150, 180, 230, 260, 300, 350, and 400°C, then cooled in a dessicator before being rapidly transferred to the Mössbauer cryostat. The spectra were recorded over 512 channels at liquid nitrogen temperature (78 K). Details of the Mössbauer spectrometer, cryogenics and data manipulation have been described elsewhere (Molloy et al., 1984). Velocity calibration was based upon natural iron and isomer shift data quoted are relative to CaSnO₃; were taken as the criterion for “goodness of fit” of data, provided the model generating the value was realistic (vide infra).

Water adsorption isotherms were determined following the method of Branson & Newman (1983) in which pre-weighed clay samples are equilibrated, at constant temperature, in dessicators containing saturated salt solutions chosen to generate a range of relative partial pressures of water from 0.0 to 0.97. In general the finely ground samples, previously heated at 150°C, required several days to reach constant weight before being transferred to the next partial pressure. Both adsorption and desorption cycles were recorded.

RESULTS

Analysis of the tin content in the Me₂SnCl₂/montmorillonite complexes prepared at pH 2.4 and 4.0 indicated that 88 and 63% of the exchange sites, respectively, were satisfied by the dimethyltin(IV) species. These figures were calculated assuming that the exchange sites were filled completely by monomeric Me₂Sn²⁺ at pH 2.4 and dimeric [Me₂SnOH]²⁺ at pH 4.0. It will be shown that there is evidence for both [Me₂SnOH]²⁺ and Me₂SnOH⁺ in the sample prepared at pH 4.0. Figure 2 shows that below 300°C the Me₂SnCl₂/montmorillonite complexes prepared at pH 4.0 maintained a larger basal spacing than that prepared at pH 2.4. The initial d-spacing of 16.0 Å, for the sample prepared at pH 4.0, is in reasonable agreement with the value of 16.6 Å reported by Petridis et al. (1989) for an analogous sample prepared at pH 5.5, in which the exchange cation was assumed to be [Me₂Sn₃(OH)₄]²⁺.

The derivative thermograms for the desorption of water from the parent Na⁺-exchanged montmorillonite and the complexes prepared using dimethyltin dichloride at pH 2.4 and 4.0 are shown in Fig. 3. Exchange with dimethyltin species resulted in the appearance of desorption maxima near 400°C. The corresponding weight losses were 1.9 and 2.9% for the samples prepared at pH 2.4 and 4.0, respectively. This behaviour is unusual insofar as inorganic cation-exchanged clays do not exhibit such a feature in the derivative thermogram (Fig. 3a) because the water loss in this region proceeds at a constant rate.

Figure 4 and the values contained in Table 1 illustrate that increasing the pretreatment temperature had a marked effect on the $^{119}\text{Sn}$ Mössbauer spectra for the Me₂SnCl₂/montmorillonite complex prepared at pH 4.0 recorded at 78 K. The spectra all consisted of
several overlapping components which were at best only partially resolved. Given that there are several possible aquated dimethyltin(IV) cations present in the exchange solution and that each of these may be distributed over a variety of different sites, it was considered reasonable to keep the number of components to the minimum consistent with interpretative integrity whilst striving to minimize \( \chi^2 \). Doublets were constrained to be symmetrical throughout, to avoid artificially good fits from strongly asymmetric components. The data presented are the culmination of an exhaustive fitting strategy from which many fits were rejected, despite low \( \chi^2 \) values, because the line-widths, \( \Gamma \), returned by the fitting routine were unrealistic. It should be noted that it would undoubtedly be possible to simulate the observed spectra from other combinations of components, so only the general picture emanating from this analysis should be considered, not minor changes in parameters.

The fitting strategy resulted in the identification of five temperature dependent components. The values presented in Table 1 illustrate how the isomer shift, \( \delta \), quadrupole splitting, \( \Delta \), line-widths, \( \Gamma \), and percentage area (\%) of these subspectra vary with pretreatment temperature. Given the complexity of the spectra, the minimal variation in the fitted values of \( \delta \) and \( \Delta \) was quite gratifying. Some difficulty was encountered in fitting the component with a contribution near 4.00 mm s\(^{-1}\) because the low-velocity wing of the doublet lay under the main, broad absorption centred around 0.12 mm s\(^{-1}\). This was
FIG. 3. Derivative thermograms for the desorption of water from Na⁺-montmorillonite (a); Me₂SnCl₂/montmorillonite complex prepared at pH 4.0 (b); and 2.4 (c).

complicated by both the weak and broad nature of the high-velocity component of this species in the samples treated at high temperature.

The water adsorption/desorption isotherms (Fig. 5) for the Me₂SnCl₂/montmorillonite complexes prepared at pH 2.4 and 4.0 are both of type IV in the Brunauer-Emmet-Teller classification and the sample prepared at pH 2.4 exhibits a large sorption capacity for water. Type IV isotherms, which are characterized by the termination of further sorption near \( P/P^0 = 1.0 \), indicate capillary condensation in a defined pore network, i.e. sorption ceases when the pore volume is filled; this behaviour pattern is more similar to that of zeolites rather than layer-silicates. Interestingly, the hysteresis on the desorption cycle was less marked and closed more rapidly in the sample prepared at pH 4.0 compared to that prepared at pH 2.4.

Base-saturated samples

Figure 6 and the values in Table 2 illustrate the extent to which the Mössbauer spectral parameters were affected when the Me₂SnCl₂/montmorillonite complex prepared at pH 4.0 was exposed to the diagnostic bases pyridine, 2-methylpyridine, 2,6-dimethylpyridine and \( n \)-butylamine. Figure 7a, which contains the derivative thermograms for the desorption of pyridine from several cation-exchanged clays, shows that the Me₂SnCl₂/montmorillonite complexes formed at pH 2.4 and 4.0 exhibit different profiles to each other and to the other cation exchange forms. This is also the case in the derivative thermograms for the desorption of \( n \)-butylamine from these cation-exchange forms (Fig. 7b). Figure 8 shows how the IR spectrum of an air-dried, pyridine-saturated sample of the Me₂SnCl₂/montmorillonite complex, prepared at pH 4.0, varied with increasing temperature. The
Fig. 4. Representative $^{119}$Sn Mössbauer spectra recorded at 78 K for the Me$_2$SnCl$_4$/montmorillonite complex prepared at pH 4.0. (a) 20°C, (b) 150°C, (c) 180°C, (d) 230°C, (e) 260°C, (f) 300°C, (g) 350°C, (h) 400°C.
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Table 1. $^{119}$Sn Mössbauer data, collected at 78 K, for the Me-SnCl$_2$/montmorillonite complex prepared at pH 4.0.
Dimethyltin cation-exchanged clays

**Fig. 5.** Water sorption (open) and desorption isotherms (closed) for the Me$_2$SnCl$_2$/montmorillonite complexes prepared at pH 2.4 (○) and 4.0 (□).

**Fig. 6.** $^{119}$Sn Mössbauer spectra recorded at 78 K for the Me$_2$SnCl$_2$/montmorillonite complex prepared at pH 4.0 after exposure to (a) pyridine, (b) 2-methylpyridine, (c) 2,6-dimethylpyridine and (d) $n$-butylamine.
TABLE 2. $^{119}$Sn Mössbauer parameters (78 K) for the Me$_2$SnCl$_2$/montmorillonite complex prepared at pH 4.0 exposed to base vapour.

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$^a$This species is only present in the absence of base. See discussion.

![Fig. 7.](image)

Fig. 7. (a) Derivative thermograms for the desorption of pyridine from Na$^+$-montmorillonite (i); acid-treated clay prepared at pH 4.0 (ii) and pH 2.4 (iii); Me$_2$SnCl$_2$/montmorillonite complexes prepared at pH 2.4 (iv) and 4.0 (v). (b) Derivative thermograms for the desorption of $n$-butylamine from Na$^+$-montmorillonite (i); acid-treated clay prepared at pH 4.0 (ii) and pH 2.4 (iii); Me$_2$SnCl$_2$/montmorillonite complexes prepared at pH 2.4 (iv) and 4.0 (v).

sample fresh from pyridine exhibited absorption bands, which, following Ward (1968), were assigned to physisorbed pyridine (1435 and 1445 cm$^{-1}$), hydrogen-bonded pyridine (1445 and 1590 cm$^{-1}$), Lewis-bound, or coordinated, pyridine (1445, 1490, 1580 and 1606 cm$^{-1}$) and the pyridinium cation (1490, 1540, 1605 and 1635 cm$^{-1}$). Degassing the sample at the beam temperature, 35°C, reduced the intensity of the 1435 and 1590 cm$^{-1}$ bands. Outgassing at 50°C resulted in further reduction of the 1435, 1580 and 1590 cm$^{-1}$ bands but, more significantly, the appearance of a strong band at 1540 cm$^{-1}$ was noted.
Fig. 8. The effect of evacuation temperature on the IR spectra of pyridine sorbed on the Me₂SnCl₂/montmorillonite complex prepared at pH 4.0. Temperatures from bottom to top are 35, 50, 100, 150 and 250°C.
After degassing at 100°C the bands near 1440 cm⁻¹ were very weak, whereas the 1540 cm⁻¹ band had grown in intensity and the poorly resolved band near 1600 cm⁻¹ had shifted to 1605 cm⁻¹. The spectra recorded at temperatures ≥150°C exhibit bands at 1490, 1540, 1605 and 1635 cm⁻¹, all of which are diagnostic of the pyridinium ion (Ward, 1968; Breen, 1991a).

DISCUSSION

The thermal stability of the dimethyltin(IV) cations in the interlamellar space in these studies is not significantly better than that reported by Petridis et al. (1989), although the Me₂SnCl₂/montmorillonite complex prepared at pH 4.0 appeared better ordered after pretreatment at 200°C (Fig. 2b) than that of Petridis et al. (1989). It would be gratifying to report that the weight losses of 1.9 and 2.9% in the thermograms for the desorption of water from the dimethyltin dichloride clay samples prepared at pH 2-4 and 4-0, respectively, (Fig. 3b,c), could be attributed solely to the loss of the methyl groups, particularly as it is near this temperature that the Mössbauer data reflect methyl group loss. However, both these percentages were too high and must therefore reflect a more complicated process which involves loss of both water and methyl groups.

Whilst the isomer shift, \( \delta \), is useful in assigning the oxidation state of tin, it is the quadrupole splitting, \( \Delta \), which yields an insight into the geometry of complexes. For alkyltin compounds of formula \( R_2SnX_2 \), the quadrupole splitting can be used as a guide to the C–Sn–C bond angle, irrespective of the coordination number at tin, assuming that only the \( R \) groups contribute to the \( \Delta \) value (Sham & Bancroft, 1975). Hence the \( \Delta \) value is \( \approx 4.00 \) mm s⁻¹ when the angle, \( \theta \), between the \( R \) groups is 180° and reaches a minimum (\( \approx 2.00 \) mm s⁻¹) when that angle is 90°. The distinction between cis- and trans-isomers of six-coordinate diorganotin compounds is one of the more celebrated applications of this methodology (Harrison, 1976). Other models for \( \Delta \)/structure correlations centre on more idealised polyhedra, but include contributions from all the coordinated ligands. For example, recent partial quadrupole splitting calculations for dibutyltin dichloride, dispersed in polyvinylchloride at 1-2 wt% (Brooks et al., 1983) have shown that \( \Delta \) for the butyl groups in trans configuration in an octahedral geometry is 3.54 mm s⁻¹. The \( \Delta \) value for butyl groups in cis configuration in trigonal bipyramidal coordination depends upon whether these groups are both in the equatorial plane (\( \theta \approx 120° \), \( \Delta = 3.07 \) mm s⁻¹) or one occupies an axial position (\( \theta \approx 90° \), \( \Delta = 2.53 \) mm s⁻¹).

Parameters arising from each of the fitted Mössbauer spectra are given in Table 1. The sample arising from the initial intercalation of the tin species into the clay at room temperature (Fig. 4a) generates a spectrum which is well simulated by two doublets, but not one or three components. Equally good fits arise from the parameters listed in Table 1 or by two tin sites with the following parameters (\( \delta \), \( \Delta \), half-width and % area): 1.18, 2.86, 1.03, 44; 1.21, 3.70, 1.09, 56. The positions of the four lines are essentially the same in the two spectra, the differences arising from which lines are paired into doublets. Similar observations have been made for the dimethyltin-exchanged clay produced at pH 5-5 (Petridis et al., 1989). In neither fit can evidence be found for the presence of the octahedral, trans-[Me₂Sn(H₂O)₄]²⁺ cation (Fig. 9e) which IR spectra suggest has a linear C–Sn–C moiety (McGrady & Tobias, 1964) hence generating a \( \Delta \) value of \( \approx 4.00 \) mm s⁻¹. Of the two possible fits to the room-temperature clay, we, like Petridis et al. (1989), prefer the fit listed in Table 1 which keeps the \( \Delta \) value for the two sites similar rather than the
alternative cited above in which the $\Delta$ values for the two components differ substantially. From the species distribution diagram shown in Fig. 1, the species present at pH 4.0 are, in order of decreasing concentration, the dimeric cation $[\text{Me}_2\text{SnOH}]^{2+}$ (Fig. 9c,d), its monomeric precursor $\text{Me}_2\text{SnOH}^+$ and the dication $[\text{Me}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+}$ (Fig. 9e) (Tobias, 1978). The last mentioned is estimated to be in low concentration, and we have already indicated that the Mössbauer spectra do not reflect the presence of such a component in the exchange clay. Infrared evidence suggests that the monomeric cation (Fig. 9a,b) contains a non-linear C–Sn–C fragment (McGrady & Tobias, 1964), although this could arise from a tetrahedral (Fig. 9a) or a trigonal bipyramidal coordination sphere (Fig. 9b) about tin. Dimerization would most probably not alter the nature of this unit, as shown in Fig. 9c,d.

The calculated C–Sn–C angles for the two species based on the $\Delta$ values (Sham & Bancroft, 1975) are 136, 138° compared with 124, 150° for the alternative fit. Our assignment of the two components is based upon spectral areas, from which the species with the slightly larger $\Delta$ value is the dimeric cation. This analysis differs from that of Petridis et al. (1989) for the analogous clay produced at pH 5.5, which assigns the two sites to the central and terminal tin atoms of a trimeric cation $[(\text{Me}_2\text{Sn})_3(\text{OH})_4]^{2+}$.

Following thermal treatment for 16 h at 120°C, a third component appears with isomer-shift and quadrupole-splitting parameters of $\approx 0.7$ and 1.7 mm s$^{-1}$, respectively. This

![Fig. 9. Selected structures for the monomeric and dimeric tin cations referred to in the discussion.](image-url)
TABLE 3. \(^{119}\text{Sn} \) Mössbauer parameter for compounds relevant to the discussion.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \delta/\text{mm s}^{-1} )</th>
<th>( \Delta/\text{mm s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SnO}_2 )</td>
<td>0.00</td>
<td>0.50</td>
</tr>
<tr>
<td>( \text{SnO} ) (black)</td>
<td>2.17</td>
<td>1.45</td>
</tr>
<tr>
<td>( \text{SnO} ) (red)</td>
<td>2.60</td>
<td>2.20</td>
</tr>
<tr>
<td>( \text{Me}_2\text{SnCl}_2 )</td>
<td>1.52</td>
<td>3.62</td>
</tr>
<tr>
<td>( \text{Me}_2\text{SnO} )</td>
<td>0.92</td>
<td>1.82</td>
</tr>
<tr>
<td>( \text{Me}_2\text{SnCl}_2 \cdot \text{(pyridine)}_2 )</td>
<td>1.27</td>
<td>3.83</td>
</tr>
</tbody>
</table>

component grew in intensity after thermal pretreatment at 150 and 180°C (Fig. 4b,c) and remained strongly in evidence even after pretreatment at 260°C (Fig. 4f,g). Table 3 indicates that these values are similar to those for \( \text{Me}_2\text{SnO} \), which appears plausible given the environment in which the tin occurs. However, caution must be exercised with this interpretation because these parameters are for pure \( \text{Me}_2\text{SnO} \) which forms polymers in the solid state. However, if \( \text{Me}_2\text{SnO} \) is present in the clay then it will almost certainly be oligomerized, if not polymerized, and thus the local geometry at tin will be the same. Petridis et al. (1989) only observed this component in samples pretreated at 80°C for 24 h, but its omission could explain the poor fit of their Mössbauer data for samples calcined at 200 and 250°C for four hours. Nevertheless, the combined results indicate that the transformation to \( \text{Me}_2\text{SnO} \) is quite slow at temperatures near 100°C.

Finally, the very characteristic isomer-shift and quadrupole-splitting values for the two components which begin to dominate the spectrum above 260°C can be attributed to \( \text{SnO}_2 \) and clearly divalent species (Fig. 4f–4h). The \( \text{SnO}_2 \) formed in the interlayer will not be the same as bulk \( \text{SnO}_2 \), which has chemically uniform tin sites. The broad line-width reflects a collection of broadly similar, but different, tin sites, which the data for \( \text{SnO}_2 \) model reasonably well. More than one site could have been used to improve the fits, but would have very little chemical (i.e. structural) validity. The changing data for the \( \text{SnO}_2 \) component reflect the changing nature of the tin environments as the sample was heated. Another contributory factor to the poor \( \chi^2 \) values associated with the fits above 260°C is the presence of small quantities of the divalent tin component which are difficult to fit because the low-velocity wing of its doublet spectrum is swamped by the contribution from \( \text{SnO}_2 \). Indeed small amounts of any unidentified phase present could result in high \( \chi^2 \) and \( \Gamma \) values. However, the high-velocity peak near 4.00 mm s\(^{-1}\), has also been observed in the \( \text{Me}_2\text{SnCl}_2 /\text{montmorillonite complex} \) prepared at pH 5.5 by Petridis et al. (1989) and by the authors in an inorganic tin-exchanged clay (Breen et al., 1992). This component is undoubtedly indicative of the presence of \( \text{Sn(II)} \) which normally gives rise to doublet spectra due to the asymmetric distribution of electron density from a stereochemically active line pair. This species seems to form along with \( \text{SnO}_2 \) around 260°C, becoming less apparent, presumably due to oxidation, at higher temperatures. This species is, however, remarkably persistent considering the treatment conditions, and is still visible even after heating at 400°C (Fig. 4h), although its inclusion in the fitting process did little to reduce \( \chi^2 \) and was thus not included. The parameters associated with the \( \text{Sn(II)} \) species are not readily equated with \( \text{SnO} \) (Table 3), the logical product given the method of preparation. The nature of this species is thus undetermined.
Having established that both Me₂SnOH⁺ and [Me₂SnOH]₂²⁺ exist up to temperatures near 200°C, consideration must be given to the nature and orientation of these species in the interlamellar space. The disappearance of resonant area associated with the dimeric dication (Fig. 9c,d) (Table 1) coincides with the accelerated decrease in the basal spacing of the Me₂SnCl₂/montmorillonite complex prepared at pH 4.0 (Fig. 2a). In contrast, the loss of the area associated with the monomeric species (Fig. 9a,b), which is less marked, has less effect on the interlayer spacing. This implies that the dimeric cation is the prime contributor to the large basal spacing.

Consideration of the structure for [Me₂SnOH]₂²⁺, drawn schematically in Fig. 10a, shows that in this five-coordinate structure one axial ligand position on each tin is satisfied by a silicate oxygen (cf. Fig. 9d) and the interaction between the methyl groups and the basal surface is minimized. If keying of the tin into the basal surface is ignored, this orientation...
would give an estimated \( d \)-spacing of 16.2 Å, which is acceptably close to the observed value of 16.0 Å (Fig. 2a). Alternative structures in which the methyl groups are directed towards the layers (cf. Figs. 9 and 5e) result in spacings which are too high (Figs. 10b,c). Not surprisingly, if a monomeric dimethyltin(IV) species, in \textit{trans}-octahedral coordination, is the dominant species in the clay, the spacing will be reduced. Calculations suggest that with the C-Sn-C axis parallel to the basal surface, the \( d \)-spacing would be 14.0 Å which is the value observed for the sample prepared at pH 2.4, after pretreatment at 200°C (Fig. 2), when most of the hydration shell water would have been removed (cf. Fig. 3).

Corroborative evidence for this interpretation was found when the isotherms presented in Fig. 5 were determined. Type IV isotherms, characterized by the termination of further sorption near \( P/P^d = 1.0 \), are usually found in structures with a well-defined pore network, i.e. sorption ceases when the pore volume is filled. This behaviour pattern is more similar to that of zeolites rather than expanding layer-silicates. When the exchange sites are occupied by the divalent Me\(_2\)Sn\(^{2+}\) cations, which are the most plentiful species at pH 2.4 (Fig. 1), there should be (i) fewer hydrophobic methyl groups to oppose water sorption, and (ii) more space available, in the \( ab \) plane, for water sorption. Furthermore, by virtue of the smaller gallery height maintained by the Me\(_2\)Sn\(^{2+}\) cations subsequent to thermal pretreatment at 150°C, it should be more difficult to desorb the occluded water than in the sample containing the large, dimeric dications with their larger gallery height after thermal pretreatment. These differences in sorptive character are certainly engendered in Fig. 5.

\textit{Base-saturated samples}

\textit{Breen et al.} (1987, 1991a,b) have shown, with the aid of corroborative IR evidence, that the maxima in the desorption profiles for pyridine and \( n \)-butylamine can be used to ascertain the types of acid site in a cation-exchanged clay. For example, in the desorption profile of pyridine from the clay acid-treated at pH 2.4 (Fig. 7a(iii)), which closely resembles that for other partially proton-treated clays (Breen, 1991a), the combination of desorption maxima near 180 and 330°C indicates the presence of Bronsted acid sites. The lack of these features in the Na\(^+\)-exchanged form indicates that no Bronsted acidity is present. The maximum in the desorption thermogram near 600°C is due to dehydroxylation of the layer. Interestingly, the Me\(_2\)SnCl\(_2\)/montmorillonite samples prepared at pH 2.4 and 4.0 exhibit a maximum near 450°C, which has not been observed previously, and disappears if the sample is heated at 350°C and then cooled prior to pyridine adsorption. Given that Mössbauer spectra of base-free samples heated at 350°C indicated that demethylation has occurred, the maximum in the pyridine desorption thermogram at 450°C is most likely associated with the interlayer dimethyltin species. The derivative thermogram for the desorption of \( n \)-butylamine from the clay acid-treated at pH 2.4 exhibited a maximum at 380°C (Fig. 7b(iii)) which can be attributed to desorption of butylamine from Bronsted sites (Breen \textit{et al.}, 1987), and was confirmed in the variable-temperature IR study (details not presented). However, neither Me\(_2\)SnCl\(_2\)/montmorillonite complexes exhibited the anticipated maximum at 380°C. Instead a complex set of desorption maxima over the temperature range 150–400°C were observed in the derivative thermogram. Clearly, the results from these derivative thermograms are qualitative, but nonetheless they do confirm that the number and type of sites are not identical in the samples prepared at pH 2.4 and 4.0.

The desorption of all four diagnostic bases was followed using variable temperature IR spectroscopy to determine the nature of the adsorption mechanism. The example of pyridine in Fig. 8 summarizes the behaviour of all these bases in that no evidence of Lewis-
bound or coordinated pyridine was seen at temperatures above 100°C. Moreover, heating
the flakes for 16 h at 250 and 400°C prior to exposure to pyridine or 2,6-dimethylpyridine
again gave no evidence of coordinated base at elevated outgassing temperatures.
Consequently, the maxima near 330°C in the derivative thermograms for the desorption of
pyridine (Fig. 7a) must be attributed to Bronsted-bound base, whereas that near 450°C
must be associated with the cation itself (e.g. demethylation) or desorption from a very
strong Bronsted site which is denatured upon thermal pretreatment at 400°C. Indeed
Petridis et al. (1989) noted that both (i) the onset of demethylation and (ii) the collapse of
the interlayer spacing occurred at higher temperatures after exposure of their sample to
ethylene glycol. They attributed this to a reduction in interlayer acidity, because the glycol
mopped up the interlayer protons, thus stabilizing the pillars. A similar process is very likely
here.

Table 2 and Fig. 6 show how the Mössbauer parameters for the Me2SnCl2/
montmorillonite sample prepared at pH 4.0 changed upon exposure to bases of different
basicities and coordinating abilities. Perhaps the most significant point is that following
exposure to base, there is more Me2SnO present than in any of the heat-treated samples and
it appears to form at the expense of the dimer, [Me2SnOH]2+. However, the IR spectra of
the pyridine-saturated Me2SnCl2/montmorillonite complex, prepared at pH 4.0, exhibits
absorption bands at 1445, 1490, 1580 and 1606 cm−1 which are diagnostic of pyridine
coordinated to a metal centre (Ward, 1968). These pyridine ligands are not strongly held,
insofar as they are desorbed by 100°C (Fig. 8), but they are clearly evident in the sample
degassed at 35°C. Thus, we have attributed the values recorded in column 1 of Table 2,
which are similar to, but nonetheless sufficiently different from, the values for Me2SnOH+,
to the change in the Mössbauer parameters when pyridine replaces a water molecule and
coordinates to tin in the monomer (Fig. 9a,b) or the dimer (Fig. 9c,d). Given that it is very
unlikely that coordination of pyridine would result in the breakdown of the dimeric dication
(Fig. 9c,d) to yield the monomer (Fig. 9a,b) we arrived at the following interpretation.
Adsorption of base in the interlamellar space results in an increase in pH which causes both
the dimerization of monomers (Fig. 9a,b) and oligomerization of the dimeric dication
(Fig. 9c,d) to form Me2SnO. Moreover, most of the remaining dimeric dication has one, or
more, of its water ligands replaced by pyridine which results in the change in quadrupole
splitting, δ, values observed in Table 2. Indeed the presence of the dimeric dication in Fig.
5a and 5c is open to debate given the statistics of the absorption. However, its inclusion,
which reduces χ2 from 1.060 to 1.030, is expedient because it prevents the δ value for
Me2SnO drifting upwards to 2.23 mm s−1 and thus allows a uniform presentation of the data
for the base-treated samples. Consequently, as there is no smooth trend in the values of δ and
Δ which parallels the increase in basicity and steric hindrance with pyridine, 2-
methylpyridine and 2,6-dimethylpyridine (pK8 = 8.75, 8.03 and 7.01, respectively) we must
conclude that some combination of basicity and steric demand occurs.

REFERENCES


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C. Breen et al.


