

## Charge Transfer Interactions in Smectite Clays

ARVIND-PAL S. MANDAIR, WILLIAM R. McWHINNIE\*

*Department of Molecular Sciences, Aston University, Aston Triangle, Birmingham B4 7ET, U.K.*

and PARISA MONSEF-MIRZAI

*Department of Chemical Engineering, Mineral Engineering Building, Elms Road, University of Birmingham, P.O. Box 363, Edgbaston, Birmingham B15 2TT, U.K.*

(Received February 24, 1987)

### Abstract

ESR and  $^{57}\text{Fe}$  Mössbauer spectroscopy are used to probe the nature of electron transfer from tetrathiafulvalene (TTF) to montmorillonite and laponite RD. Evidence for electron transfer to structural iron(III) is found for montmorillonite. If the clay is exchanged with a transition metal ion such as copper(II) or vanadyl(IV), TTF may react preferentially with the interlamellar ion.

$[\text{TTF}]_3(\text{BF}_4)_2$  will ion exchange with sodium laponite but during the process much of the crystallinity of the clay is destroyed.

Disc conductivities of sodium montmorillonite and sodium laponite are enhanced by an order of magnitude on intercalation with TTF; the conductivity is believed to be ionic in origin. Exchange with  $[\text{TTF}]_3(\text{BF}_4)_2$  gives no enhancement to the disc conductivity of sodium laponite.

### Introduction

It is well known that benzidine will interact with clays such as montmorillonite by transfer of an electron and intercalation of the benzidine cation. An elegant  $^{57}\text{Fe}$  Mössbauer study [1] showed that structural iron(III) accepted the electron to become reduced to iron(II). Some years ago we conceived the idea that other electron donors might enter into charge transfer interactions with smectite clays and decided to study the intercalation of organometallics by smectite clays. A major objective was (and remains) a study of the intercalation of organotellurium compounds [2], but we decided to start with a study of tetrathiafulvalene (TTF). However, during the course of this work a paper was published by Van Damme *et al.* [3] which described results on the intercalation of TTF with smectite clays in which the major techniques used were XRD, IR and

UV spectroscopy. Interestingly, the genesis of the idea was the same in both groups.

On reviewing our results in this general area, it occurred to us that we had some data which were complementary to those of the French workers since we had used mainly Mössbauer and ESR spectroscopy; also we had carried out experiments with clays exchanged with transition metal ions and, in addition, had investigated ion exchange reactions with  $[\text{TTF}]_3(\text{BF}_4)_2$ . We now report briefly on these extra data which, fortunately, largely support the earlier conclusions [3].

### Experimental

#### Materials

Two clays, montmorillonite and a synthetic hectorite, were used. The montmorillonite was obtained from Berk Limited ( $\text{SiO}_2$ , 52.2;  $\text{Al}_2\text{O}_3$ , 12.8;  $\text{Fe}_2\text{O}_3$ , 10.2;  $\text{TiO}_2$ , 0.6;  $\text{MgO}$ , 0.5;  $\text{CaO}$ , 2.2;  $\text{K}_2\text{O}$ , 0.4;  $\text{Na}_2\text{O}$ , 0.1;  $\text{H}_2\text{O}$  ( $<105^\circ\text{C}$ ), 12.3;  $\text{H}_2\text{O}$  ( $>105^\circ\text{C}$ ) 6.6%. Cation exchange capacity, 80 meq 100  $\text{g}^{-1}$ ). The montmorillonite was converted to the sodium form prior to use. The hectorite was laponite RD (manufactured by Laport Ltd.) and was virtually free of paramagnetics. It was used in the sodium form (cation exchange capacity = 70 meq 100  $\text{g}^{-1}$ ). For some experiments laponite was exchanged with  $\text{Cu}^{2+}$  (via  $\text{CuCl}_2 \cdot \text{H}_2\text{O}$  in aqueous solution) and with  $\text{VO}_2^{2+}$  (via  $\text{VO}_2\text{SO}_4$  in aqueous solution). Tetrathiafulvalene (TTF) was obtained from Aldrich Chemical Co.  $[\text{TTF}]_3(\text{BF}_4)_2$  was prepared following the literature [4].

#### Reactions with Clays

Following a range of experiments in which the influence of light, temperature and contact time between the clay and TTF was evaluated, the procedure adopted was as follows. Clay (1 g, montmorillonite or laponite in  $\text{Na}^+$  form) was stirred with acetonitrile (15  $\text{cm}^3$ ) for 15 min in a two

\*Author to whom correspondence should be addressed.

TABLE I. ESR Data for Clays Treated Either With TTF or With  $\text{TTF}_3(\text{BF}_4)_2$ 

Clay	Colour prior to treatment	<i>g</i> value	Colour following treatment	<i>g</i> value
$\text{Na}^+$ montmorillonite	yellow	v. broad (iron(III))	dark brown	2.005 <sup>a</sup> (weak)
$\text{Cu}^{2+}$ montmorillonite	yellow/green	2.102	dark brown	2.008 <sup>a</sup>
$\text{Na}^+$ laponite	white		white	
$\text{Cu}^{2+}$ laponite	blue	$g_{\parallel} = 2.264$ $g_{\perp} = 2.015$	dark brown	2.005 <sup>b</sup>
$\text{VO}_2^+$ laponite	green	$g_{\parallel} = 1.944$ $g_{\perp} = 1.948$	light brown	$g_{\parallel} = 1.939^c$ $g_{\perp} = 1.948$
$\text{Na}^+$ hectorite (natural Californian)	white		light brown	
$\text{Na}^+$ laponite	white			
(i) 40 meq. $\text{TTF}_3(\text{BR}_4)_2$			purple/brown	2.007
(ii) 60 meq			purple/brown	2.005
(iii) 80 meq			purple	2.005
$\text{TTF}_3(\text{BF}_4)_2$	purple	2.007		

<sup>a</sup>Broad signals. <sup>b</sup>Sharp. <sup>c</sup>Some reduction in relative intensity compared with untreated clay.

necked round bottomed flask. A weighed quantity of TTF (in the range 0.1–3.0 mmol) was dissolved in the minimum volume of acetonitrile and added to the flask and heated under gentle reflux. (In separate experiments it was established that sodium montmorillonite assumed, to the eye, a constant colour after a reaction period of 4 h. The exclusion of light made no difference to our observations.) The clays treated under these conditions were: sodium montmorillonite, copper(II) montmorillonite, sodium laponite, copper(II) laponite, vanadyl(IV) laponite and, for comparison, sodium hectorite (prepared from hectorite obtained from Hector, Calif.). We found that constant physical data (ESR *g* values, Mössbauer parameters) were obtained at clay/TTF loadings of 1.0–1.5 mmol TTF per mmol clay. Table I presents qualitative observations on the change of clay appearance during the reaction; also included are ESR data (*vide infra*).

#### Ion Exchange Reactions with $[\text{TTF}]_3(\text{BF}_4)_2$

Ion exchange capacities of clays are expressed in units of meq  $100 \text{ g}^{-1}$ , hence five solutions of  $[\text{TTF}]_3(\text{BF}_4)_2$  in acetonitrile prepared by dissolving a known weight of the salt and making up to  $25 \text{ cm}^3$  in volumetric flasks such that, when contacted with 0.1 g clay, the solutions were equivalent to 40, 50, 60, 70 and 80 meq  $100 \text{ g}^{-1}$  of the clay. The clay selected was sodium laponite (0.1 g) which was heated under gentle reflux with the full  $25 \text{ cm}^3$  of the above solutions. Release of sodium ions was monitored by flame photometry. Thus following separation of the clay by centrifuging, the acetonitrile solution, combined with two further  $25 \text{ cm}^3$  aliquots of acetonitrile used to wash the clay, was analysed for sodium. A calibration curve was constructed from measurements on sodium iodide

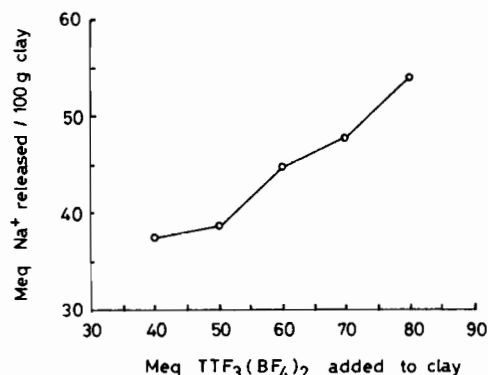


Fig. 1. Sodium release curve.

solutions in acetonitrile. The sodium release as a function of salt concentration is given in Fig. 1. ESR data are given in Table I.

#### Physical Measurements

X-ray powder diffraction studies were made with a Phillips automatic powder diffractometer with  $\text{Cu K}\alpha$  radiation. Electron spin resonance (ESR) data were obtained with a JEOL PE-1X instrument. *g* Values were determined relative to a  $\text{Mn}^{2+}/\text{MgO}$  standard. Diffuse reflectance spectra (UV-Vis) were obtained with a Pye-Unicam SP 800 instrument.  $^{57}\text{Fe}$  Mössbauer spectra were measured with a constant acceleration spectrometer of standard design. Isomer shifts are relative to iron metal. The Mössbauer data are given in Table II.

Measurements of electrical conductivity were made by pressing the TTF doped clays into discs (10 tonne hydraulic pressure) the dimensions of which were measured with a micrometer ( $\pm 0.001 \text{ mm}$ ). The faces of the discs were sputter coated

TABLE II.  $^{57}\text{Fe}$  Mössbauer Parameters for Montmorillonites Before and After Treatment With TTF

Clay	$^{57}\text{Fe}$ Mössbauer parameters		Origin
	$\delta^a$ ( $\text{mm s}^{-1}$ )	$\Delta^b$ ( $\text{mm s}^{-1}$ )	
Na <sup>+</sup> montmorillonite	0.36	0.45	iron(III)
	0.38	1.06	iron(III)
Na <sup>+</sup> montmorillonite <sup>c</sup> , TTF (experiment A)	0.36	0.48	iron(III)
Na <sup>+</sup> montmorillonite <sup>c</sup> , TTF (experiment B)	0.36	0.44	iron(III)
	1.13	2.52	iron(II)
Na <sup>+</sup> fuller's earth	0.43	0.86	iron(III)
	0.27	0.42	iron(III)
Na <sup>+</sup> fuller's earth <sup>c</sup> , TTF	0.36	0.54	iron(III)

<sup>a</sup>Isomer shift vs. metal (all data obtained at room temperature).<sup>b</sup>Quadrupole splitting.<sup>c</sup>Treated with 1 mmol TTF.TABLE III. Disc Conductivities of Clays Before and After Treatment With TTF or TTF<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub>

Sample	Conductivity ( $\Omega^{-1}\text{cm}^{-1}$ )	Sample	Conductivity ( $\Omega^{-1}\text{cm}^{-1}$ )
Na <sup>+</sup> montmorillonite	$6.7 \times 10^{-9}$	Na <sup>+</sup> montmorillonite/TTF (1.5 mmol)	$4.3 \times 10^{-8}$
		Cu <sup>2+</sup> montmorillonite/TTF (1.5 mmol)	$3.1 \times 10^{-8}$
Na <sup>+</sup> laponite	$8.4 \times 10^{-9}$	Na <sup>+</sup> laponite/TTF (1.5 mmol)	$5.2 \times 10^{-8}$
		Na <sup>+</sup> laponite/TTF <sub>3</sub> (BF <sub>4</sub> ) <sub>2</sub> 70 meq	$3.5 \times 10^{-9}$
		Na <sup>+</sup> laponite/TTF <sub>3</sub> (BF <sub>4</sub> ) <sub>2</sub> 80 meq	$9.4 \times 10^{-9}$

with 99.9% aluminium and thin gold wires were attached using silver paste. Three to five current readings were taken for each sample in the potential range 4.00 to 20.00 V. Data are given in Table III. Measurements were also made on undoped clays.

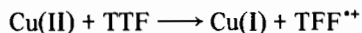
## Discussion

The UV-Vis data that we obtained parallel exactly those reported previously [3] and hence are not tabulated or discussed. Our XRD data were obtained on specimens equilibrated with the laboratory atmosphere and which were consequently not anhydrous. In a typical experiment the basal (001) spacing of sodium montmorillonite on treatment with TTF increased from 13.46 to 20.08 Å of which the intercalation of TTF can be shown to contribute a minimum of 6.6 Å. It is probable, particularly in the light of the IR results of Van Damme *et al.* [3], that the molecular plane of the TTF is perpendicular to that of the clay. In the remainder of this discussion we concentrate on data which are new for the clay/TTF system.

## ESR Data

Table I indicates that, generally, a colour change to brown occurs on treating montmorillonite with TTF. This is also true of hectorite a natural clay, but laponite – a synthetic hectorite essentially iron free – shows no change on intercalation of TTF; however if laponite is used in the Cu<sup>2+</sup> or VO<sup>2+</sup> form rather than the Na<sup>+</sup> form, distinct colour changes are seen. A parallel ESR study showed that constant *g* values were obtained from clay specimens treated with 1 mmol TTF/mmol of clay and the data in Table I are these constant values. For Na<sup>+</sup> montmorillonite a very broad iron(III) signal is seen but after treatment with 1 TTF a new signal at *g* = 2.005 is superimposed. For Cu<sup>2+</sup> montmorillonite, the Cu(II) is detectable as a broad isotropic signal at *g* = 2.102 but this is removed on TTF treatment and is replaced by a new signal at *g* = 2.008. Na<sup>+</sup> laponite gives no ESR signal before or after TTF treatment; however Cu<sup>2+</sup> laponite gives a well resolved anisotropic spectrum typical of tetragonal copper(II). Treatment with TTF totally removes this signal and replaces it with a strong, sharp signal at *g* = 2.005. It is clear that a redox reaction has

occurred between Cu(II) and TTF in both montmorillonite and laponite:



There is no clear evidence from the radical  $g$  values that Cu(I) and TTF<sup>•</sup> are coordinated. Vanadyl laponite showed a colour change on treatment with TTF but no unambiguous ESR evidence for TTF radicals was seen; a reduction in the vanadyl signal intensity was noted as was a slight modification to the value of  $g_{\parallel}$ . The ESR data show that organic radicals may be generated either by reaction with interlamellar transition metal ions (laponite and Cu<sup>2+</sup> montmorillonite) or with structural iron (montmorillonite).

### <sup>57</sup>Fe Mössbauer Spectra

In their study of the interaction of benzidine with montmorillonite, Thomas *et al.* [1] used a clay which contained both structural iron(III) and iron(II). It was noted that on treatment with benzidine the iron(II) doublet ( $\delta = 1.36$ ,  $\Delta = 2.77$  mm s<sup>-1</sup>) increased in intensity at the expense of the iron(III) doublet ( $\delta = 0.59$ ,  $\Delta = 0.65$  mm s<sup>-1</sup>). These observations illustrated the value of Mössbauer spectroscopy to detect charge transfer to structural iron(III).

The Mössbauer spectrum of our Na<sup>+</sup> montmorillonite was fitted to two doublets (Table II), the inner doublet ( $\delta = 0.36$ ,  $\Delta = 0.45$  mm s<sup>-1</sup>) being more intense (approximately 2:1) than the outer doublet ( $\delta = 0.38$ ,  $\Delta = 1.06$  mm s<sup>-1</sup>). The goodness of fit ( $\chi^2$  values) and the parameters were not significantly altered by constraining either only areas or areas and widths of the lines. The width of the peaks ( $\Gamma_{1/2}$ ) was considerable, *i.e.* 0.6–0.8 mm s<sup>-1</sup>. No structural iron(II) was detected in this sample montmorillonite. The two doublets have often been observed for montmorillonite samples [5] and an interpretation which has gained acceptance suggests the larger quadrupole splitting to arise from iron(III) in *trans*-O<sub>4</sub>(OH)<sub>2</sub> sites (M1) and the smaller from iron(III) in *cis*-O<sub>4</sub>(OH)<sub>2</sub> sites (M2). This is certainly consistent with the point charge model [6]. However, a recent electron diffraction study of a Wyoming montmorillonite showed that 75–100% of the M1 sites were occupied by iron(III) [7], thus the assignment of the most intense doublet to M2 sites is unlikely to be correct. Cardile and Johnson [8] have reassessed the Mössbauer data for montmorillonites and have shown that the fit obtained is to some extent a function of the constraints with the fitting program; they point out that since the iron content of montmorillonite is low the Mössbauer parameters will be sensitive to variations in the geometrical arrangement of neighbouring cations and even to the more distant interlamellar ions. The two doublet fit is then in a sense of fortuitous con-

sequence of a continuum of  $\delta$  and  $\Delta$  values for individual iron(III) sites.

On treatment with TTF results of varying consistency were obtained, thus in some experiments (B, Table II) definite evidence of the generation of iron(II) was obtained ( $\delta = 1.13$ ,  $\Delta = 2.52$  mm s<sup>-1</sup>). However, more usually (A, Table II) only a modified iron(III) spectrum was seen. Significantly better  $\chi^2$  values were obtained by a fit to one broad iron(III) doublet (this is also true for the iron(III) resonance in experiment B). These data accord with the view of Cardile and Johnson that the spectrum will be influenced by near and more distant ions; also the measured basal spacing is likely to be a factor. The data are also consistent with the view that there is indeed a small degree of charge transfer from TTF to structural iron(III), although this is not always adequate to produce sufficient iron(II) to be detectable by Mössbauer spectroscopy.

We had available a specimen of fuller's earth which was in the Na<sup>+</sup> form. A Mössbauer study showed a close parallel to the montmorillonite work. The only significant difference was that in the TTF treated sample the intensity of the component of the doublet at higher velocity was lower than the lower velocity component. This may reflect the presence in the fuller's earth of small quantities of tetrahedral iron(III) which we did not allow for in the fitting procedure.

### Experiments with [TTF]<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub>

We had hoped to observe enhanced conductivities for TTF treated clays and felt that ion exchange of [TTF]<sub>3</sub><sup>2+</sup> might enhance the 'TTF' loading of the clay – it was also a way of obtaining some TTF radical character for laponite. The sodium release curve (Fig. 1) shows that ion exchange proceeds to approximately 75% completion on treating the laponite with 80 meq of [TTF]<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub>. (We also monitored the intensity of the spectra of [TTF]<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub> in the supernatant with similar conclusions.) An ESR study (Table I) showed that at lower salt concentrations (40 meq 100 g<sup>-1</sup> clay) the  $g$  value of the separated clay was identical to that of the crystalline salt (2.0066). As the salt concentration increased and the proportion ion exchanged increased a  $g$  value of 2.005 was observed for the clay, *i.e.* identical with those seen for other systems detailed in Table I (*vide supra*). These data reflect the fact that sorption on the crystal surface is probably a precursor to ion-exchange.

The diffuse reflectance spectrum of the exchanged laponite is dominated by a broad band at 480 nm which does not correlate well with any band seen in the acetonitrile solution spectrum of [TTF]<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub>. It is known that the salt contains trimeric [TTF]<sub>3</sub><sup>2+</sup> ions [9] but it is not certain that the same species exists in the interlamellar region of laponite.

Nor, despite the identity of  $g$  values to those seen for intercalated TTF, does the reflectance spectrum parallel those of the TTF intercalates which have as their dominant band a peak at 435 nm [3].

XRD data were both disappointing and surprising in that there was no indication of the low angle reflections normally observed for phyllosilicates. The very broad bands obtained indicated lack of a crystalline phase and resembled those obtained from a calcined clay. We are unable to comment therefore on the orientation of the intercalated species.

#### Disc Conductivities

In contrast to Van Damme *et al.* [3], we did observe an order of magnitude increase in conductivity on treatment of the clays with TTF (Table III). Almost certainly the mechanism for the conduction is ionic and we speculate that the mobility of the interlamellar ions may be increased by the increase in the basal spacing. Certainly we cannot attribute the increase to the charge transfer process since Na<sup>+</sup> laponite/TTF for which there is no evidence of charge transfer does show the same enhancement of conductivity as the other clays.

By contrast, the [TTF]<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub> exchanged laponite shows no increase in conductivity.

#### Acknowledgements

One of us (A.-P.M.) thanks Aston University for a studentship. We also thank Dr F. J. Berry of the University of Birmingham for the Mössbauer spectra of the fuller's earth specimens.

#### References

- 1 D. T. B. Tennakoon, T. M. Thomas and M. J. Tricker, *J. Chem. Soc., Dalton Trans.*, 20, 2211 (1974).
- 2 H. B. Singh, W. R. McWhinnie, R. F. Ziolo and C. H. W. Jones, *J. Chem. Soc., Dalton Trans.*, 1267 (1984).
- 3 H. Van Damme, F. Obrecht and M. Letellier, *Nouv. J. Chim.*, 8, 681 (1984).
- 4 F. Wudl, *J. Am. Chem. Soc.*, 97, 1962 (1975).
- 5 I. Rozenson and L. Heller-Kallai, *Clay. Clay Miner.*, 25, 94 (1977).
- 6 G. M. Bancroft, 'Mössbauer Spectroscopy, An Introduction for Inorganic Chemists and Geochemists', McGraw Hill, Maidenhead, UK, pp. 122.
- 7 S. I. Tsipursky and V. A. Drits, *Clay Miner.*, 19, 177 (1984).
- 8 C. M. Cardile and J. H. Johnson, *Clay. Clay Miner.*, 34, 307 (1986).
- 9 K. Veyama, G. Masuboyashi, R. Shimizu and T. Tanaka, *Polyhedron*, 4, 1783 (1985).