Chem. Mater. 1992, 4, 522–529

Articles

Macroanionic Electron Acceptors for the Synthesis of Low-Dimensional Organic Conductors: Synthesis and Structural Characterization of Iron Oxychloride Intercalated with Tetraselenafulvalene, Bis(ethylenedithio)tetrathiafulvalene, and Bis(pyrazino)tetrathiafulvalene

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Received May 6, 1991. Revised Manuscript Received January 6, 1992

The synthesis and structural characterization of FeOCl intercalated with the organic donors tetraselenafulvalene (TSF), bis(ethylenedithio)tetrathiafulvalene (ET), and bis(pyrazino)tetrathiafulvalene (BPTTF) are reported. X-ray powder diffraction studies of both microcrystalline powders and oriented films of the intercalates have been used to assess intercalate structure. Intercalation of the donor TSF into FeOCl results in the intercalate $\mathrm{FeOCl(TSF)}_{1/8.5}$, with lattice parameters a = 3.786 (5) Å, b = 3.323 (2) Å, and c = 26.98 (2) Å. In $\mathrm{FeOCl(TSF)}_{1/8.5}$, the donors are aligned with their molecular planes parallel to the interlayer c axis. Reaction of the electron donor ET with FeOCl in dimethoxyethane (DME) results in the intercalate $\mathrm{FeOCl{\cdot}(ET)}_{1/4}$, with lattice parameters a = 3.783 (5) Å, b = 3.307 (4) Å, and c = 44.76 (1) Å. This intercalate exhibits a remarkably large interlayer spacing of 22.4 Å. The ET donors are probably oriented within their long axes slightly canted from the perpendicular to the FeOCl layers. The BPTTF intercalate has a stoichiometry of $\mathrm{FeOCl(BPTTF)}_{1/20}$, with the planar BPTTF molecules lying parallel to the FeOCl sheets.

Introduction

Low-dimensional organic conductors[1-12] are formed from the combination of planar aromatic or heteroaromatic electron donors (e.g., tetrathiafulvalene (TTF),[2] bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET))[3] and electron acceptors (e.g., tetracyanoquinodimethane (TCNQ)[4]) or simple anions (e.g., PF_6^-). These materials crystallize as segregated stacks of donors and acceptors. Overlap of their π-systems along the stacks results in the formation of supramolecular orbitals (i.e., bands) in one or two dimensions, thereby creating a pathway for conduction electrons. While a number of salient features of low-dimensional organic conductors have been recognized, the two most prominent are that: (i) the donors and acceptors be crystallized in *segregated* stacks (crystallization in mixed stacks results in electrically insulating materials) and (ii) the average oxidation state of the molecules in the stacks be nonintegral (i.e., partial charge transfer between the stacks).[1d]

In an attempt to prepare new organic conducting materials, we have explored the use of layered inorganic hosts as macroanionic electron acceptors to provide a matrix that enforces a segregated stack structure upon the organic π-donors. Intercalation chemistry[13,14] provides a synthetic method for the introduction of organic π-donors into the matrix of lamellar transition-metal hosts.[15,16] This method appears to be well suited to the synthesis of organic conductors since (i) intercalation intrinsically enforces the formation of the segregated donor/acceptor structure necessary to produce electrically conducting materials

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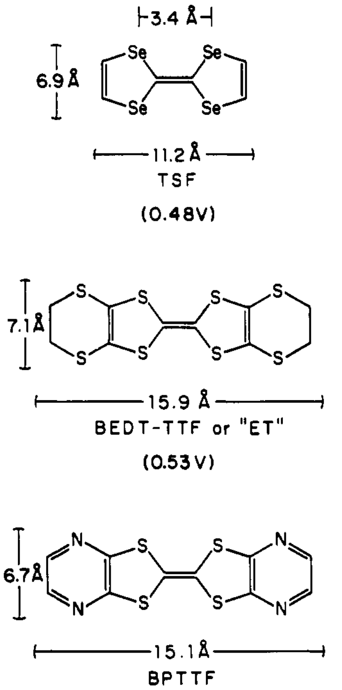

Figure 1. Schematic drawings of the molecules intercalated into FeOCl illustrating approximate dimensions. Numbers in parentheses are reduction potentials of the monocation vs SCE.[22]

(requirement 1 above) and (ii) the vast majority of intercalation reactions occur with some degree of charge transfer from the guest (i.e., the organic π-donor) to the host (i.e., the layered matrix) during the intercalation process.[13] The degree of charge transfer between donor and acceptor can then in principle be controlled by chemical modification of the host or guest species.

An intercalation chemistry of the organic π-donors TTF[16] and related tetrathiolenes[17] and of various aromatic hydrocarbons[15a,18] has been established in our laboratory for the layered host iron oxychloride, FeOCl. The desired host–guest structural orientation is observed for these intercalates, resulting in the formation of stacks of organic donors separated by FeOCl layers.[17d] Unfortunately, however, the reactions were found to proceed with essentially complete charge transfer from guest to host[17b,17e] and, in the case of TTF, to result in sulfur–sulfur contacts at distances greater than the sum of the van der Waals radii and thus in poor orbital overlap.[17c] These factors prevent the formation of a metallic conduction band within the guest layers, and the resulting materials are invariably semiconducting. TTF has also been intercalated into V_2O_5[19] and smectic clays (hectorite, montmorillonite, and glauconite),[20] displaying a similar stacking orientation; TTF was also found to be fully oxidized in these materials, but their conductivities were not reported. In an analogous approach, pyrrole was intercalated into FeOCl, apparently resulting in the formation of a conducting polypyrrole within the interlayer region.[21]

In an attempt to obtain a partial degree of charge transfer from guest to host and thus to increase the likelihood of metallic conductivity within the guest layers, we have investigated the intercalation chemistry of several analogues of tetrathiafulvalene, including tetraselenafulvalene (TSF), tetramethyltetraselenafulvalene (TMTSF), BEDT-TTF (ET), and bis(pyrazino)tetrathiafulvalene (BPTTF) (Figure 1). These materials are particularly promising since they are poorer electron donors than TTF[22] and might therefore form intercalates in which the guest stacks are partially oxidized. The intercalation of these molecules into FeOCl results in the following phases: $\mathrm{FeOCl(TSF)}_{1/8.5}$, $\mathrm{FeOCl(ET)}_{1/4}$, and $\mathrm{FeOCl(BPTTF)}_{1/20}$. The synthesis and some properties of the selenium intercalates $\mathrm{FeOCl(TMTSF)}_{1/10}$ and $\mathrm{FeOCl(TSF)}_{1/8.5}$ have been described elsewhere,[17a] while a brief communication on the ET intercalate $\mathrm{FeOCl(ET)}_{1/4}$ has appeared.[23] Herein, the synthesis and structural characterization of the ET and BPTTF intercalates are described together with further structural results on the TSF intercalate.

Experimental Section

FeOCl was prepared as reported;[24] the purity of the material was assessed by X-ray powder diffraction (XPD) and elemental analysis. TSF was prepared by modifications[25b] of published procedures.[25a] BEDT-TTF[26] and BPTTF[27] were prepared as described; these materials were purified by column chromatography and recrystallization prior to use.

Preparation of Intercalates. Intercalates were routinely prepared and handled under an inert atmosphere of dry nitrogen or argon (unless otherwise indicated). Microcrystalline solids were filtered using anaerobic glass frits; the solutions and slurries were transferred via wide-bore cannula. All solvents were distilled from appropriate drying agents and degassed just prior to use.

Experimental techniques concerning the preparation of intercalates have been published previously.[17] The intercalates reported herein were prepared in a similar manner. Where X-ray

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powder diffraction indicated incomplete intercalation, the solid was treated with a fresh solution of the intercalant. Finely divided FeOCl starting material was obtained by sonication of microcrystalline FeOCl in dry toluene for 20 min at a power of 50 W. The absence of the characteristic FeOCl interlayer reflection[28] was used to verify complete intercalation. The conditions of the reactions are given below.

FeOCl(TSF)$_{1/8.5}$: FeOCl was treated with a solution of 0.1 M TSF in dimethoxyethane (DME) (3:1 mole ratio FeOCl:TSF) for 17 days at 85 °C. The resulting black microcrystalline solid was then washed anaerobically with DME until the eluant became colorless, and the solid was dried in vacuo at room temperature. XPD: d = 13.45 Å. Chemical ionization mass spectrometry (CIMS): m/z = 393 and 197, assigned to (TSF)H$^+$ and (TSF)H^{2+}, respectively. Elemental Anal. % found (calcd) Fe 36.18 (36.14); Cl 23.23 (22.94); Se 24.96 (24.64); C 5.62 (5.62); H 0.49 (0.31).

FeOCl(ET)$_{1/4}$: FeOCl was treated with a 0.05 M solution of ET in DME (2:1 mole ratio FeOCl:ET) for 21 days at 85 °C. The resulting black microcrystalline solid was washed with DME and dried in vacuo. XPD: d = 22.35 Å. CIMS: m/z = 385, assigned to (ET)H$^+$. Elemental Anal. % found (calcd) Fe 27.26 (26.96); Cl 18.0 (17.12); S 32.52 (32.18); C 15.01 (15.08); H 1.03 (1.00).

FeOCl(BPTTF)$_{1/20}$: FeOCl (0.340 g; 3.2 mmol) was treated with 0.266 g (0.86 mmol) of BPTTF in 15 mL of DME at 85 °C for 30 days. BPTTF is only sparingly soluble in organic solvents, so that at room temperature most remained in suspension. The solids were then washed with DME and dichloromethane until the eluant was colorless and the resulting black microcrystalline solid was dried in vacuo. CIMS revealed the presence of small amounts of DME co-intercalated with BPTTF (m/z = 309 ((BPTTF)H$^+$) and 91 (DME)H$^+$)). DME was removed by heating the intercalate in vacuo at 160 °C for 1–2 days. XPD: d = 11.101 Å. CIMS: m/z = 309. Elemental Anal. % found (calcd) Fe 45.11 (45.52); Cl 28.36 (28.89); S 5.58 (5.22); C 5.22 (4.89); N 2.29 (2.28).

X-ray Diffraction. X-ray powder diffraction data were obtained on a Guinier camera (Enraf-Nonius Model FR552) and a Scintag XDS-2000 diffractometer. A Cu X-ray source equipped with a graphite monochromator to provide clean Kα_1 radiation was employed to collect diffraction data photographically. Silicon was used as an internal standard for all samples. Film from the camera was read using a Huber Model 622 film reader capable of 0.001-mm accuracy. Cell parameters were refined by the least-squares method.

Oriented films of the intercalates were prepared by suspending the samples in chloroform and allowing the suspensions to dry slowly on X-ray sample slides under an inert atmosphere. XPD peak profiles of oriented films of the intercalates were obtained using a Scintag XDS-2000 diffractometer. Errors in the intensities of low-angle reflections as a result of the slit width (1°) were left uncorrected. This fact is at least, in part, responsible for the high-R values reported. Data were routinely refined using programs provided by Scintag. Integrated peak intensities were obtained by three methods and averaged as outlined in the Scintag powder diffraction manual. The intensities were corrected for the Lorentz and polarization factors $1/\sin 2\theta$ and $(1 + \cos^2 2\theta)/2$, respectively. To calculate structure factors, thermal parameters were set at Fe = 1.0, O = 2.0, Cl = 1.5, C = 3.0, S, Se = 2.0.

Synthesis

Intercalation reactions involve the diffusion of guest species across relatively large distances. The intercalation rate is therefore dependent upon a number of physical parameters, such as the surface area and particle size of the host, host–guest, and guest–guest interactions, defects, and interlayer impurities.[13,29] The intercalation of TSF into FeOCl at 85 °C in DME requires approximately 17 days for completion. However, other intercalants require much longer times (4–6 weeks). The slow rate of these reactions is mainly a result of the poor solubility of the donors in DME but may also be due in part to their poor electron-donating ability relative to TSF (see Figure 1). The intercalation of TMTSF into FeOCl is particularly slow;[17a] in some cases, even after several weeks, intercalation is not complete as determined by X-ray powder diffraction. We have found that the intercalation rate can be increased by employing finely divided FeOCl, obtained by sonication of the pristine host in dry toluene just prior to reaction, as a starting material. Complete intercalation of TMTSF into FeOCl can then be achieved within ca. 3 weeks. The product obtained by this method is chemically and spectroscopically identical to that obtained previously.[17a] Ultrasound has previously been employed to increase the rate of intercalation reactions,[30] apparently by increasing host surface area and not by forcing the guest into the interlayer region. Thus, sonication of the host may be performed prior to intercalation, rather than in situ.

Intercalation of the organic donors used to form organic metals into FeOCl has been shown to proceed via a redox mechanism;[15–17,31] thus, intercalation into FeOCl is strongly dependent upon the reducing power of the guest species. Aromatic hydrocarbon donors with an ionization potential ≤7.15 eV intercalate into FeOCl readily, whereas those with an ionization potential ≥7.15 eV do not.[18] During the intercalation process, electrons are transferred from the guest species to the host matrix. The intercalation rate is therefore highly dependent upon the basicity of the solvent used. Intercalation reactions were carried out using a variety of solvents, including benzene, toluene, acetonitrile, and DME. In each case it was found that DME was the best solvent for facilitating the reaction. It has been suggested[32] that DME facilitates electron transfer from the guest to the host by stabilization of radical cations generated during the redox process. The solvent clearly plays a role in the intercalation process: TMTSF intercalates FeOCl completely in DME, whereas no reaction occurs when benzene, toluene, or acetonitrile are used as the solvent.[17a] DME was found to be incorporated into the BPTTF intercalate, resulting in the phase FeOCl(BPTTF)$_{1/20}$(DME)$_{1/50}$. However, DME deintercalates at lower temperatures than BPTTF and could be selectively removed by heating the material in vacuo at 160 °C.

Structural Studies

Structural information is paramount to the understanding of solid-state materials such as intercalation compounds, where questions concerning host–guest and guest–guest orientations must be addressed. Single-crystal X-ray diffraction studies of intercalated materials are often not possible, since well-formed single crystals are difficult or impossible to obtain. X-ray powder diffraction does provide, however, a direct and accurate method of measuring interlayer distances in intercalated materials, from which relative host–host and host–guest orientations may be inferred. However, X-ray scattering is dominated by heavy atoms (i.e., the host layers), and hence this method usually gives no direct information on the position or orientation of the guest species.

Such information can be obtained, however, through X-ray powder diffraction studies of oriented microcrystalline films of intercalated materials.[32] The microcrystalline platelets of intercalated materials are easily oriented with their c axes parallel to one another and perpendicular to a surface by suspending the specimen in a dense solvent

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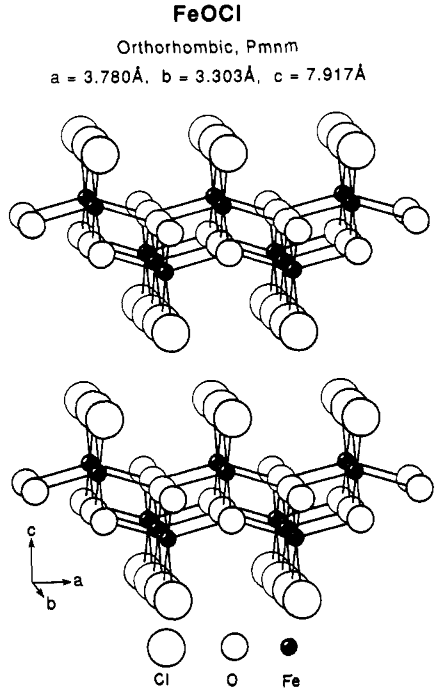

Figure 2. Illustration of two layers of the FeOCl structure (adapted from ref 13e).

(e.g., CCl_4 or $CHCl_3$), applying the suspension to an X-ray sample slide and allowing the suspension to slowly dry under an inert atmosphere. The preferred orientation results in enhancement of the intensities of X-ray reflections having a large interlayer component (e.g., $00l$ reflections). The structure factors of these reflections can be derived from their intensities through the relation $F(l) = (I/LP)^{1/2}$, where L and P are the Lorentz and polarization correction factors. A Fourier synthesis of the structure factors can then be used to compute the electron density of the intercalate along the interlayer c axis. Host–guest orientations can then be inferred by assigning peaks in the electron density to heavy atoms. Various orientations can then be checked by comparing the calculated goodness-of-fit (R) for each orientation. The signs of the phases of the structure factors were determined solely as a contribution of the scattering of the FeOCl layers. This assumption is almost certainly valid for $FeOCl(TTF)_{1/8.5}$, given the small occupancy of guest species (1 TTF/8.5 FeOCl units) and the relatively heavy atoms of the host matrix. For the intercalates $FeOCl(TSF)_{1/8.5}$ and $FeOCl(ET)_{1/4}$, the scattering contribution of the guest species is expected to be larger, since TSF contains four heavy atoms and ET has a relatively large occupancy within the FeOCl layers. The XPD data obtained from these materials were initially phased as discussed above and then rephased to include the scattering of the guest species. Only minor changes in the signs of the phases occurred upon inclusion of the guest in the model, suggesting that the assumption that the signs of the phases is determined predominantly by the scattering of the host layers is valid. To calculate structure factors, the guest occupancy within the interlayer region was fixed at the value obtained from elemental analyses. The results of these studies and X-ray powder diffraction studies of unoriented microcrystalline powders are presented below.

Table I. Calculated and Observed Structure Factors for $FeOCl(TTF)_{1/8.5}$

l	$F(l)$ calcd[a]	$F(l)$ calcd[b]	$F(l)$ obsd
1	69.1	49.1	123.4
2	16.7	28.4	95.3
3	−0.8	−3.2	0.0
4	10.1	6.1	13.9
5	6.7	13.5	42.1
6	−21.9	−26.5	38.3
7	−45.9	−45.2	86.1
8	−39.6	−36.7	52.6
9	−13.2	−19.1	32.1
10	5.2	12.3	23.0
11	4.7	−0.3	2.0
12	−0.1	1.1	5.5

[a] Includes scattering of FeOCl layers only. [b] Includes contribution of the guest species; $R = 0.282$. R calculated as $R = \sum(K|F_o| - |F_c|)/\sum K|F_o|$.

Results and Discussion

FeOCl Structure. The FeOCl structure (Figure 2) has been discussed in detail previously.[13e,17d] The structure consists of double layers of distorted, edged-shared $FeO_{4/4}Cl_{2/2}$ octahedra, in which the chloride anions are cis-coordinated so that they are outermost on either side of the layers. Only relatively weak van der Waals bonding interactions exist between the layers.

The internal structure of the individual layers of FeOCl is not perturbed significantly upon intercalation. The small perturbations that do result can be correlated to electronic factors as a result of charge transfer from guest to host accompanying the intercalation process.[12c,d] Extended X-ray absorption fine structure and neutron powder diffraction studies of FeOCl intercalates have shown that the Fe–O and Fe–Cl bond distances do not change significantly upon intercalation.[17c,d]

The relative orientations of two adjacent layers may, however, change upon intercalation.[33] This orientation is determined by the specific host–guest interactions of the intercalates and the steric packing constraints imposed by the guest.

Intercalate Structure. The X-ray powder patterns of the intercalates were indexed using a body-centered unit cell and are consistent with orthorhombic space groups *Immm* or *I*222. Extinctions observed in the diffraction data could be accounted for by a doubling of the c axis. The arrangements of the chloride sheets consistent with a doubling of the c axis have been discussed in detail by Phillips and Herber.[33b] In each case, the data are consistent only with a lateral shift of the layers in the $a-b$ plane of $a/2$ and $b/2$, leaving the chloride ions of adjacent layers eclipsed. This model was first proposed by Halbert and Scanlon[33a] for metallocene intercalates of FeOCl and appears to be quite general for molecular intercalates of FeOCl.[14–18]

To assess the validity of the method of determining c-axis atomic positions from electron density projections, it was first tested on $FeOCl(TTF)_{1/8.5}$, in which the orientation of TTF is known from neutron powder diffraction studies.[17c] The X-ray powder diffraction peak profile of an oriented film of this material contained 12 $00l$ reflections to $d = 1.083$ Å. The interlayer separation determined from these reflections was 12.993 (7) Å, in good agreement with that reported previously (13.009 Å).[17c] The signs of the phases of the structure factors derived from the intensities of the $00l$ reflections were assigned solely based upon the contributions of the FeOCl layers. A Fourier synthesis of the electron density then provided the projection of the electron density along the interlayer axis shown in Figure 3a; the observed and calculated structure

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(33) (a) Halbert, T. R.; Scanlon, J. C. *Mater. Res. Bull.* **1979**, *14*, 415. (b) Phillips, J. E.; Herber, R. H. *Inorg. Chem.* **1986**, *25*, 3081.

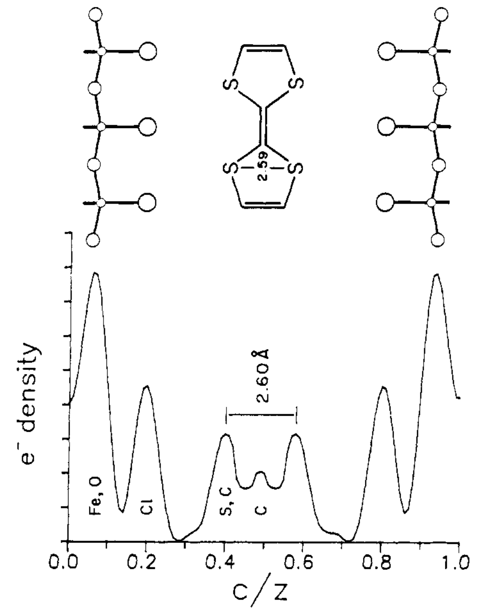

Figure 3. (a, bottom) Projection of the electron density of FeOCl(TTF)$_{1/8.5}$ along the interlayer axis. (b, top) Illustration of the orientation of TTF as deduced from the electron density; Fe = small circles, O = medium circles, Cl = large circles.

Table II. XPD Data for FeOCl(TSF)$_{1/8.5}$ (a = 3.786 (5) Å, b = 3.323 (2) Å, c = 26.98 (3) Å)

hkl	*d*(obsd), Å	*d*(calcd), Å	I^a
002	13.47	13.49	s
004	6.761	6.746	w
103	3.485	3.490	vs
105	3.101	3.099	vw
015	2.834	2.830	w
017	2.516	2.517	w
112	2.455	2.456	m
114	2.344	2.343	w
200	1.891	1.893	m
220	1.871	1.875	w
$11\underline{10}$	1.832	1.833	m
020	1.662	1.662	m
022	1.650	1.649	m
215	1.574	1.573	w
217	1.512	1.513	m
303	1.249	1.250	m
222	1.243	1.243	m

^{a} Relative intensity: vs = very strong, s = strong, ms = medium strong, w = weak, vw = very weak.

factors are given in Table I. The orientation of the TTF molecule derived from the projection is represented graphically in Figure 3b. Two large peaks assigned as a contribution of sulfur and carbon clearly establish a perpendicular orientation of the TTF molecule, which agrees with that reported earlier.[17b,c] The observed S–S distance (2.60 Å) is in excellent agreement with the 2.59 Å intraring distance observed in the TTF molecule (Figure 1). The sulfur–chloride distance of 3.52 Å calculated from the electron density map is somewhat longer than that reported previously[17c] for FeOCl(TTF)$_{1/8.5}$ (S··Cl = 3.32 Å). The former distance, however, is in better agreement with S··Cl distances observed in conducting TTF salts that contain chloride anions, e.g., (TTF)Cl$_{0.92}$, S··Cl = 3.51 Å; (TMTTF)FeCl$_4$, S··Cl = 3.48 Å.[17c]

FeOCl(TSF)$_{1/8.5}$. Seventeen independent reflections were observed in the X-ray powder diffraction data (Table II) of microcrystalline powders of FeOCl(TSF)$_{1/8.5}$. The interlayer distance of 13.47 Å represents an increase of 5.6 Å over that in pristine FeOCl (7.917 Å). This expansion is approximately 1.3 Å less than the height of the TSF molecule (Figure 3)[34] and is consistent with an orientation of the molecular plane of TSF perpendicular to the FeOCl layers, but slightly interpenetrating the corrugated chloride sheets of FeOCl. A slight interpenetration of the guest species into the host lattice is quite common in intercalation compounds.[13-20]

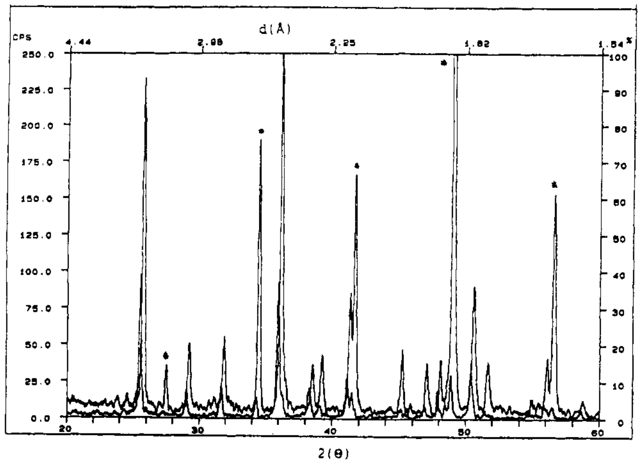

Figure 4. XPD peak profiles of an oriented film (upper profile) and microcrystalline powder (lower profile) of FeOCl(TSF)$_{1/8.5}$ in the region 2θ = 20–60°; 00l reflections are indicated by asterisks.

Table III. Calculated and Observed Structure Factors for FeOCl(TSF)$_{1/8.5}$ (Scale Factor K = 0.468, R = 0.223)

	$F(l)$			$F(l)$	
l	calcd	obsd	l	calcd	obsd
1	39.7	89.1	8	−25.8	43.2
2	28.8	99.2	9	−35.4	63.8
3	11.3	28.7	10	7.0	17.7
4	−14.3	28.2	11	10.4	16.4
5	28.1	80.7	12	−9.7	10.9
6	−20.2	37.9	13	12.1	17.2
7	−50.0	97.3	14	5.3	6.5

The interring Se–Se distance of 3.4 Å in TSF fortuitously approximates the intralayer Cl–Cl distance along b (3.303 Å) in FeOCl. In the case of TTF, it has been suggested[17b–e] that there is significant interaction between the "soft" sulfur atoms of the TTF molecule and the chloride sheets of the host lattice. This interaction essentially locks the FeOCl layers into place. Taking these features into account and imposing this model upon FeOCl(TSF)$_{1/8.5}$, it is possible to calculate a stoichiometry of FeOCl(TSF)$_{1/8.5}$ for close-packed TSF molecules within the interlayer space, which is very near that observed (FeOCl(TSF)$_{1/8.5}$) and allows us to conclude that the TSF molecules are very nearly close-packed (nearly 94% of the available space is filled) within the interlayer region.

Figure 4 shows the X-ray powder diffraction peak profiles in the region 2θ = 20–60° for both an oriented film and a microcrystalline powder of FeOCl(TSF)$_{1/8.5}$. The enhancement of the 00l reflections (marked by asterisks) can clearly be seen. Fourteen 00l reflections to d = 0.9611 Å were observed. The interlayer separation calculated from these reflections is 13.455 (6) Å, in excellent agreement with that obtained from an unoriented sample. A Fourier synthesis of the structure factors derived from the intensities of the 00l reflections provided the projection of the electron density along c shown in Figure 5a; the observed and calculated structure factors are given in

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(34) The distances shown are those observed in the radical cations, calculated from the following references. TTF: Dahm, D. J.; Johnson, G. R.; May, F. L.; Miles, M. G.; Wilson, J. D. *Cryst. Struct. Commun.* **1975**, *4*, 673. TSF: Johannsen, I.; Bechgaard, K.; Kindorf, G.; Thorup, N.; Jacobsen, C.; Mortensen, K. *Synth. Met.* **1986**, *15*, 333.

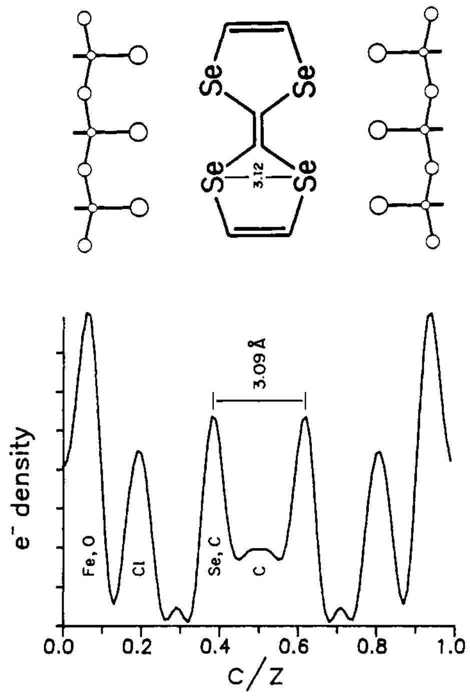

Figure 5. (a, bottom) Projection of the electron density of $FeOCl(TSF)_{1/8.5}$ along the interlayer axis. (b, top) Illustration of the orientation of TSF as deduced from the electron density; Fe = small circles, O = medium circles, Cl = large circles.

Table III. It was found that the signs of only two phases changed upon inclusion of the TSF molecule in the structure. The projected electron density shown in Figure 5a is consistent only with an orientation of the TSF molecules perpendicular to the FeOCl layers, as represented graphically in Figure 5b. Two large peaks observed in the interlayer region are assigned as contributions of Se and C. The Se–Se distance observed (3.09 Å) is in excellent agreement with the *intra*ring Se–Se distance found in the TSF radical cation (3.12 Å).[34] The Se··Cl distance calculated from this model is 3.59 Å, less than the sum of their respective van der Waals radii (3.65 Å).[23] This is not surprising since Se–anion contacts in, for example, $(TMTSF)_2X$ salts are known to be well within the sum of their van der Waals radii.[1a,d]

$FeOCl(ET)_{1/4}$. The observed and calculated X-ray powder diffraction data for $FeOCl(ET)_{1/4}$ are presented in Table IV. Twenty-two 00*l* reflections were observed in the X-ray powder diffraction pattern of a oriented film of this intercalate, allowing for a high degree of accuracy in determining the interlayer distance, calculated to be 22.35 (3) Å. This represents an expansion of 14.43 Å over that of pristine FeOCl. Considering the dimensions of the ET molecule (Figure 1), a number of orientations of intercalated ET molecules are possible based on these data alone, including (i) ET molecules oriented perpendicular to the host lattice with the long axis of ET parallel to *c*, (ii) a double layer of ET molecules perpendicular to the layers but with their central C=C bonds parallel to the layers, and (iii) a triple layer of ET molecules lying parallel to the host layers. These models were chosen after a careful review of the structures of $(ET)_2X$ salts[35] and are necessarily reminiscent of the packing of ET molecules observed in these salts. Given the large interlayer expansion observed for $FeOCl(ET)_{1/4}$, the relative host–guest and guest–guest orientations are probably dominated by the packing preferences of ET molecules.

Table IV. XPD Data for $FeOCl(ET)_{1/4}$ (a = 3.783 (5) Å, b = 3.307 (4) Å, c = 44.76 (1) Å)

hkl	*d*(obsd), Å	*d*(calcd), Å	I^a
002	22.18	22.38	s
004	11.156	11.190	vs
006	7.435	7.460	s
$00\underline{12}$	3.7307	3.7300	m
103	3.6679	3.6670	m
105	3.4849	3.4846	w
013	3.2280	3.2286	w
$00\underline{14}$	3.1931	3.1971	s
$01\underline{11}$	2.5627	2.5663	w
$10\underline{13}$	2.5456	2.5463	w
$01\underline{13}$	2.3804	2.3851	m
$11\underline{12}$	2.0711	2.0708	w
200	1.8917	1.8915	m
$00\underline{24}$	1.8648	1.8650	m
$00\underline{26}$	1.7220	1.7215	m
020	1.6542	1.6535	m
217	1.5905	1.5903	w

[a] Relative intensity: see footnote to Table II.

A significant deviation from planarity occurs in the ET molecule due to the presence of the saturated ethylene substituents at each terminus of the molecule, which play an important role in determining the structure and electrical properties of $(ET)_2X$ conductors.[9d] A result of the nonplanarity is that little or no columnar stacking, as observed in other organic metals, is observed in the $(ET)_2X$ salts. Instead, the structures are dominated by a corrugated sheet network of S–S interactions, which result in the formation of a two-dimensional conduction band in a plane that contains the "stacking" axis.[1a,3a] These interactions are conceivably possible in all of the structural models presented above for $FeOCl(ET)_{1/4}$, since the columnar stacking important for virtually all other organic conductors is not a requisite for metallic conductivity in the $(ET)_2X$ systems.

The validity of the above models can be checked by comparing the observed stoichiometry against the calculated close-packed limit. The stoichiometries calculated for close-packed ET molecules in models i–iii are $FeOCl(ET)_{1/4}$, $FeOCl(ET)_{1/6}$, and $FeOCl(ET)_{1/3}$, respectively. Thus, only models i and iii are plausible by this criterion. Furthermore, the third model requires the presence of a substantial amount of empty space in the interlayer region and therefore seems unlikely, since no molecular intercalates are known in which ordered empty space is present in the interlayer region.[13a]

The X-ray powder diffraction data of both microcrystalline powders and oriented films of $FeOCl(ET)_{1/4}$ showed a remarkable contribution of 00*l* reflections, suggesting a high degree of order along the *c* axis. The structure factors derived from the intensities of the 00*l* reflections were initially phased considering scattering from the FeOCl layers only. However, the projection of the electron density was not in accord with the expected model i discussed above. The data could be fit, however, by canting the ET molecules at an angle of ca. 15° from the perpendicular with respect to the FeOCl layers. This orientation is similar to that observed in the conducting salts $(ET)_2BrO_4$[36] and $(ET)_2ReO_4$,[3c] in which the ET molecules are canted at an angle of ca. 10° from the perpendicular with respect to the anion sheets. Rephasing the data according to this model and a subsequent Fourier synthesis of the electron density along the *c* axis gave the projection shown in Figure 6a. The observed and calculated structure factors are

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[35] References 1a and 9–12 and references therein.

[36] Williams, J. M.; Beno, M. A.; Wang, H.-H.; Reed, P. E.; Azevedo, L. J.; Schirber, J. E. *Inorg. Chem.* **1984**, *23*, 1790.

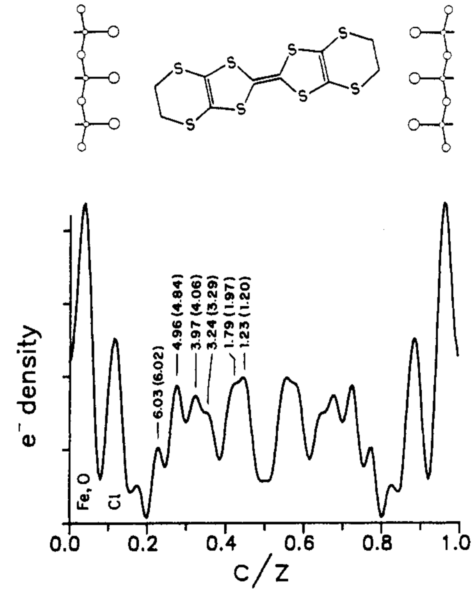

Figure 6. (a, bottom) Projection of the electron density of FeOCl$(ET)_{1/4}$ along the interlayer axis. Numbers are distances in angstroms from the origin (taken as the midpoint of the projection). Numbers in parentheses are the corresponding distances in the ET molecule. (b, top) Illustration of the orientation of ET as deduced from the electron density; Fe = small circles, O = medium circles, Cl = large circles.

Table V. Structure Factors of FeOCl$(ET)_{1/4}$ Derived from the Intensities of 00*l* Reflections and Those Calculated for the Perpendicular and Canted Models of FeOCl$(ET)_{1/4}$

	structure factors		
(00*l*)	derived[a] $[I/(LP)]^{1/2}$	calcd ($\theta = 0°$)[b]	calcd ($\theta = 15°$)[c]
2	42.8	39.6	37.5
4	67.7	44.4	46.9
6	74.0	45.8	47.3
8	16.0	14.3	12.0
10	3.0	-3.5	-6.1
12	9.9	-17.8	-9.7
14	40.7	41.4	27.9
16	3.5	-11.5	-2.2
18	20.0	6.2	9.4
20	28.5	-6.8	-17.3
22	25.3	-35.9	-33.4
24	40.6	-51.5	-45.7
26	47.1	-48.9	-42.4
28	25.8	-6.7	-34.1
30	17.2	-46.2	-21.1
32	9.6	-6.0	-7.1
34	1.5	21.0	6.1
36	13.8	-3.1	7.4
38	0.0	3.9	3.6
40	15.3	-3.8	-1.2
42	1.2	13.5	-3.6
44	15.2	-9.1	13.9
		$R = 0.471$	$R = 0.245$

[a] I = intensity; L and P are the Lorentz and polarization correction factors discussed in the text. [b] Structure factors calculated for ET oriented perpendicular to the FeOCl layers. [c] Structure factors calculated for ET canted at 15° from the perpendicular with respect to the FeOCl layers.

given in Table V. The structural model proposed for FeOCl$(ET)_{1/4}$ is schematically represented in Figure 6b, along with the observed and calculated atomic distances relative to the origin (chosen as the midpoint of the interlayer separation). Structure factors were calculated for both model i and the variation of i with ET canted at 15° from the perpendicular, resulting in R values of 0.471 and 0.245, respectively.

Table VI. XPD Data for FeOCl$(BPTTF)_{1/20}$ (a = 3.781 (4) Å, b = 3.313 (3) Å, c = 22.02 (5) Å)

hkl	*d*(obsd), Å	*d*(calcd), Å	I^a
002	11.010	11.010	s
006	3.668	3.670	m
103	3.340	3.362	m
011	3.248	3.277	m
200	1.887	1.890	s
202	1.868	1.863	m
020	1.657	1.657	m
$11\underline{10}$	1.650	1.650	w
121	1.515	1.514	w
123	1.485	1.486	w

[a] Relative intensity: see footnote to Table II.

The nonplanarity of the ethylene substituents in the ET molecule introduces structural and electronic complexity in $(ET)_2X$ systems. For example, anion size and hydrogen–anion interactions determine the conformation (staggered or eclipsed) of the ethylene groups.[9d] Given the structural complexity of these systems, the atomic positions derived from the projection of the electron density along the interlayer axis should be viewed with caution. It is possible that two (or even three) crystallographically independent ET molecules reside within the interlayer space of FeOCl; projection of the electron density along the interlayer axis may not be a reliable method for determining guest orientation in this case.

FeOCl$(BPTTF)_{1/20}$. The observed and calculated XPD data for FeOCl$(BPTTF)_{1/20}$ are given in Table VI. The diffraction lines were relatively broad, indicating a poor degree of crystallinity in the intercalate. The calculated interlayer distance, 11.010 Å, represents an increase of 3.10 Å over that of pristine FeOCl. This expansion is approximately 0.5–0.6 Å less than the van der Waals thickness of BPTTF and allows the conclusion that the BPTTF molecules are parallel to the FeOCl layers. The stoichiometry calculated for such an orientation is FeOCl$(BPTTF)_{1/20}$, in agreement with that observed.

The molecular structure of BPTTF is very similar to that of ET. Furthermore, the structures of $(BPTTF)_2X$ salts[37] are decidedly two-dimensional, as are the $(ET)_2X$ salts. Therefore, it might be expected that the BPTTF molecules would have an orientation similar to that of ET in FeOCl$(ET)_{1/4}$. However, N··H–N hydrogen-bonding interactions may play a role in determining the orientation of BPTTF within the FeOCl layers; trace amounts of H_2O may serve as the source of protons. Such interactions apparently determine the orientations of NH_3[38] and pyridine[39] within the layered host TaS_2 and of NH_3 within TiS_2.[40] In these materials, the nitrogen lone pair is directed in between the host layers, and adjacent molecules are hydrogen bonded to one another. This model would require that the BPTTF molecules be oriented parallel to the FeOCl layers, since this is the only possible orientation in which such interactions could occur.

Conclusions

The syntheses of intercalation compounds of FeOCl have been qualitatively evaluated based on a number of criteria.

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(37) (a) Pappavassilliou, G. C.; Yiannopoulos, S. Y.; Zambounis, J. S. *J. Chem. Soc., Chem. Commun.* **1986**, 820. (b) Kikuchi, K.; Kamio, H.; Saito, K.; Yiannopoulos, S. Y.; Pappavassiliou, G. C.; Kobayashi, K.; Ikamoto, I. *J. Chem. Soc. Jpn.* **1988**, *61*, 741.

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Table VII. Structural Parameters for FeOCl and the Intercalates

compound	interlayer dist,[a] Å	interlayer expansion, Å	nesting,[b] Å	orientation
FeOCl	7.917			
FeOCl(TSF)$_{1/8.5}$	13.45	5.6	1.3	perpendicular
FeOCl-(TMTSF)$_{1/10}$	13.79	5.9	1.3	perpendicular
FeOCl(ET)$_{1/4}$	22.35	14.4	1.7	perpendicular[c]
FeOCl-(BPTTF)$_{1/20}$	11.01	3.1	0.6	parallel

[a] Where possible the interlayer distances were calculated from XPD data of oriented films. [b] Nesting refers to the interpenetration of the guest species into the FeOCl layers. [c] See text.

It appears that DME is the solvent of choice to carry out intercalation reactions of FeOCl that proceed by a redox process and that ultrasound is a useful tool for facilitating the rate of these reactions.

X-ray powder diffraction studies of both microcrystalline powders and oriented films of the intercalates have been used to address the question of host–guest and guest–guest orientations in the intercalation compounds FeOCl(TSF)$_{1/8.5}$ and FeOCl(ET)$_{1/4}$. Structural parameters for FeOCl and the intercalates are summarized in Table VII. Comparison of the observed stoichiometries of the intercalates with the maximum stoichiometries calculated for close-packed guest molecules reveals that the latter are nearly close-packed within the FeOCl layers.

In FeOCl(TSF)$_{1/8.5}$ (and FeOCl(TMTSF)$_{1/10}$[17a]), the donors are apparently aligned with their molecular planes parallel to the *a* axis. This model, originally proposed for FeOCl(TTF)$_{1/8.5}$ based on XPD, EXAFS, and neutron powder diffraction studies,[17c–e] places the TSF (and TMTSF) molecules in stacks along the *b* axis at an intrastack distance of 3.79 Å (equal to the *b*-axis parameter of FeOCl), which is within the sum of the van der Waals radii of Se (3.85 Å). Typical intra- and interstack Se–Se distances in conducting (TMTSF)$_2$X salts (X = AsF$_6^-$, BF$_4^-$) are 3.7–4.0 Å.[2c,41] This suggests that Se–Se overlap in FeOCl(TSF)$_{1/8.5}$ and FeOCl(TMTSF)$_{1/10}$ may be sufficient to result in the formation of a band in the interlayer region. The observation of a perpendicular host–guest orientation in FeOCl(TMTSF)$_{1/10}$[17a] (vs parallel in FeOCl(TMTTF)$_{1/12}$[17b]) further supports this model.

Intercalation of the electron donor ET into FeOCl results in the intercalate FeOCl(ET)$_{1/4}$, which exhibits a remarkably large interlayer distance of 22.35 Å. Furthermore, this intercalate contains a much greater guest occupancy ($^1/_4$) compared with other FeOCl intercalates (e.g., FeOCl(TTF)$_{1/8.5}$[17b]). This result would not be expected based on the size of the guests, since the ET molecule is much larger than TTF, and clearly suggests that the guest arrangement in FeOCl(ET)$_{1/4}$ is unique among these intercalates. Projections of the electron density along the interlayer axis suggest that ET is probably oriented with its molecular plane perpendicular to the FeOCl layers and its long axis canted at an angle of ca. 15° from the perpendicular.

The host layers of FeOCl display a remarkably elastic adaption to the size, the preferred orientations and the packing preferences of the organic guest molecules. Indeed, a major conclusion derived from these observations is that the specific host–guest and guest–guest orientations in these materials are largely dictated by the stacking preferences and steric packing constraints of the guest molecules. These factors are apparently dominant in determining intercalate structure, in that the energy needed to separate the layers is more than compensated for by an energetically favorable packing of the guest molecules. For example, the orientation of the organic π-donor that minimizes the energy of the system with respect to the layers (i.e., gives smallest possible expansion) would invariably be a parallel one, with the planar organic donors lying flat and an interlayer expansion equal to the van der Waals thickness of the aromatic π-system (ca. 3.4–3.8 Å). With the exception of FeOCl(BPTTF)$_{1/20}$ (and FeOCl(TMTTF)$_{1/12}$[17b]), this orientation is not observed. On the contrary, FeOCl(ET)$_{1/4}$ displays an interlayer expansion of 14.4 Å. Given these arguments, it is likely that the structures of the organic π-donors within the galleries of FeOCl closely resemble those observed for their corresponding organic salts. For these reasons, the use of lamellar materials as macroanionic acceptors appears to be highly suited to the preparation of low-dimensional conductors.

Fourier transform infrared spectroscopic studies and temperature-dependent conductivity measurements have also been performed on these materials and will be described elsewhere.

Acknowledgment. This research was supported in part by the U.S. National Science Foundation, Solid State Chemistry, Grant No. DMR-8313252, and by the North Atlantic Treaty Organization (NATO) Grant No. 0727/87. We thank R. F. Bryan for helpful discussions concerning the analysis of the X-ray data.

Registry No. TSF, 54489-01-9; ET, 66946-48-3; BPTTF, 97942-32-0; FeOCl(TSF)$_{1/8.5}$, 124505-64-2; FeOCl(ET)$_{1/4}$, 127103-45-1; FeOCl(BPTTF)$_{1/20}$, 140468-31-1; FeOCl, 13870-10-5; FeOCl(TMTSF)$_{1/10}$, 124505-65-3.

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