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STRUCTURAL STUDIES OF FeOCl INTERCALATED WITH TETRATHIAFULVALENE AND RELATED MATERIALS

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Abstract For FeOCl and its intercalates, $FeOCl{\cdot}TTF_{1/9}$ (TTF=tetrathiafulvalene), $FeOCl{\cdot}TTN_{1/9}$ (TTN=tetrathianaphthalene), and $FeOCl{\cdot}TTT_{1/7}$ (TTT= tetrathiatetracene), the combination of X-ray powder diffraction data and Fe K-edge EXAFS (Extended X-ray Absorption Fine Structure) spectroscopy provides a consistent picture of the structural changes of the FeOCl host upon intercalation. A structural model based upon the data obtained from both techniques is discussed, in which the intercalated radical cations are tilted at an angle θ from the b axis ($\theta=25\pm5°$ for TTF, $42\pm5°$ for TTN, TTT). In the TTN and TTT intercalates, the radical cations are also tilted at an additional angle ϕ from the ac plane ($\phi=14\pm5°$).

INTRODUCTION

The occurence of high conductivity in low-dimensional materials is dictated at least in part by structural constraints. There are basically three categories of well-studied low-dimensional conducting materials: (i) those containing linear chains of transition metals; (ii) linear polymers; and (iii) those containing stacks of donor and acceptor molecules. Compounds such as $K_2Pt(CN)_4{\cdot}0.3Br{\cdot}3H_2O$ (Krogmann's salt) fall into the first category; in these materials, it is the overlap of transition metal d-orbitals that provides a pathway for electrical condition.[1] In the case of linear polymers such as $(SN)_x$ and $(CH)_xX_y$, electrons can travel both along and between the chains of atoms.[2] Finally, materials containing stacks of donor and acceptor molecules are typified by TTF-TCNQ, whose high conductivity can be attributed to the presence of segregated stacks of TTF(donor) and TCNQ(acceptor) molecules.[3] Compounds of this general type that crystallize as mixed stacks are usually insulators.[4] By using layered materials such as FeOCl as a host lattice, intercalated molecules such as TTF can, in principle at least, be forced to orient themselves so that they are stacked within the inorganic host with the possibility of substantial intermolecular π-orbital overlap. Thus, provided that this structural criterion can be met, intercalation chemistry may prove to be an attractive route to new low-dimensional conducting materials, given the synthetic flexibility available with various electron donors and hosts. In this paper, we report the results of EXAFS and X-ray diffraction studies that indicate that the desired orientation of intercalants is achieved for TTF, TTN, and TTT in FeOCl.

EXPERIMENTAL

The TTF, TTT, and TTN intercalates of FeOCl were prepared by minor modifications of the procedures previously reported.[5] X-ray powder diffraction data were obtained on a G.E. automated diffractometer using Co(Kα; 1.79021Å) radiation; platinum metal was used as an internal standard. Iron K-edge EXAFS spectra were measured at the Cornell High Energy Synchrotron Source (CHESS). The data were measured in the transmission mode on samples diluted with boron nitride, and analyzed at Bell Laboratories as previously described[6], using pristine FeOCl as the model compound.

RESULTS AND DISCUSSION

Single crystal[7] and powder[8] X-ray diffraction measurements have shown that the crystal structure of FeOCl is orthorhombic (space group Pmnm), with a = 3.780Å, b = 7.917Å, and c = 3.303Å. The structure consists of an $(FeO)_n^+$ sheet with a layer of chloride ions above and below. Along the a axis the iron atoms are bridged by two oxygen atoms, while along c the bridging atoms are a chloride and an oxygen. The b axis corresponds to the interlayer spacing.

In order to determine the structure of the intercalates, information obtained from X-ray powder diffraction was combined with iron K-edge EXAFS (Extended X-ray Absorption Fine Structure) spectroscopic data. X-ray powder diffraction provides information on the long range order of the material, whereas EXAFS spectroscopy examines the local environment of an absorbing atom. Both the TTF and TTN intercalates are well-ordered solids, as shown by both the number of Bragg reflections and the fits obtained for the X-ray powder diffraction data (Table I). In contrast, the X-ray powder pattern for $FeOCl(TTT)_{1/7}$ could not be fit as well; this may be due to the fact that TTT is significantly bulkier than either TTF or TTN, resulting in decreased order and broader (1-2Å greater than for pristine FeOCl) reflections. The X-ray powder data for $FeOCl(TTF)_{1/9}$ could be fit with a monoclinic cell in which the c axis corresponds to the interlayer distance. Both $FeOCl(TTN)_{1/9}$ and $FeOCl(TTT)_{1/7}$ are orthorhombic and exhibit a significant (~7.5Å) expansion of the b axis (the interlayer distance) compared to pristine FeOCl. Analysis of the EXAFS

TABLE I Observed and calculated X-ray diffraction data for FeOCl intercalates.*

$FeOCl(TTF)_{1/9}(C_7H_8)_{1/22}$				$FeOCl(TTN)_{1/9}(C_7H_8)_{1/21}$				$FeOCl(TTT)_{1/7}$			
I	d_{obs}	d_{calc}	hkl	I	d_{obs}	d_{calc}	hkl	I	d_{obs}	d_{calc}	hkl
100	13.08	13.205	001	100	15.43	15.43	010	100	15.32	15.32	010
20	6.60	6.602	002	50	7.73	7.72	020	25	8.03	7.660	020
10	3.475	3.480	200	<1	5.15	5.14	030	5	5.45	5.416	120
<1	3.079	3.075	$\bar{4}05$	<1	3.09	3.09	050	2	3.39	3.323	201
<1	2.742	2.739	$\bar{2}15$	<1	3.03	3.07	130	<1	2.66	2.708 2.617	240 151
1	2.636	2.641	005	<1	2.58	2.57	060	<1	2.40	2.393	250
6	2.493	2.491	$\bar{4}03$	<1	2.51	2.52	101	<1	1.99	2.028	062
1	2.338	2.337	014	<1	2.15	2.14	160	<1	1.89	1.900	170/410
1	1.880	1.886	007	1.0	1.94	1.95	151	<1	1.76	1.713	280
<1	1.811	1.833	016	<1	1.89	1.90	210				
1	1.644	1.651	008	1	1.72	1.72	180				
2	1.505	1.45	220	<1	1.68	1.67	202				
				<1	1.58	1.58	231				

FeOCl(TTF): β = 115° a = 3.84 x 2
b = 3.31 c = 14.43

FeOCl(TTN): a = 3.83 b = 15.43 c = 3.34

FeOCl(TTT): a = 3.83 x 2 b = 15.32
c = 3.34

*The X-ray data were fit using peak positions only; relative intensities and apparent extinctions were not considered.

data indicates that the Fe-nearest neighbor (O, Cl) distances are essentially unchanged upon intercalation, but that the Fe---Fe distance along a increases by 0.05 - 0.06Å upon intercalation, compared to the value of 3.780Å in pristine FeOCl. This requires a slight decrease in the O-Fe-O angle and moves the chloride ions further apart along a.

To determine the orientation of an organic molecule such as TTF, TTN, or TTT within the FeOCl host, it is necessary to consider the interaction of the intercalants with the chloride layers. Before intercalation, a chloride ion in one layer is nested in a hole formed by four almost close-packed chloride ions of the layer below. Intercalation results in a large expansion of the FeOCl lattice along the b-axis, which a much smaller expansion along the a-axis; adjacent layers may or may not be shifted laterally with respect to one another. Since the dimensions of the organic intercalants are known[9,10] and the structure of the host has been determined from EXAFS and X-ray measurements, adequate information is available to determine the orientation of the intercalants.

The distance between sulfur atoms in adjacent rings in TTF is 4.4Å[9]. If one sulfur atom rests in a hole formed by four chloride ions of an FeOCl layer, then the sulfur on the adjacent ring must occupy the next hole along the a-axis, because of the (fortuitous) approximate match between the S---S distance and the repeat distance along a. This arrangement is based on an excluded volume argument; inspection of models shows that the TTF molecule cannot align itself in any other direction without serious disruption of the FeOCl structure. Alignment of TTF along a thus minimizes steric repulsion between the intercalant and the chloride layer, but results in stretching of the lattice along a due to the ~0.6Å mismatch between host and intercalant. Given the observed expansion of the interlayer distance (5.7Å), the plane of the TTF molecule (width across ring = 6.7Å) must be tilted by an angle $\theta = 25 \pm 5°$ with respect to the perpendicular to the chloride layers (Figure 1 (top)). The X-ray powder diffraction data support this model. Also, one of the chloride layers must shift laterally

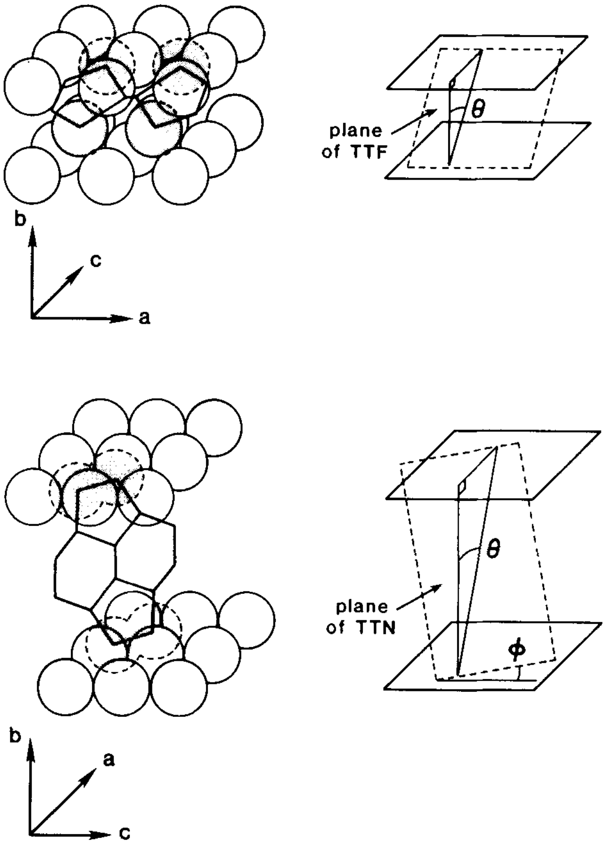

FIGURE 1. Schematic drawing of the orientation of TTF (top) and TTN or TTT (bottom) in FeOCl.

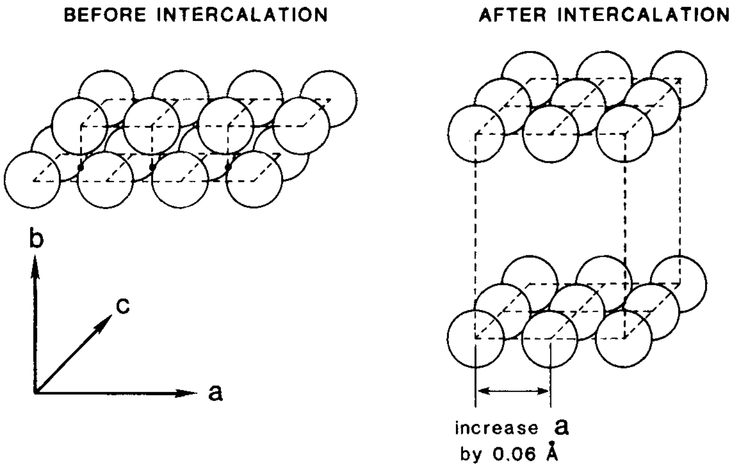

FIGURE 2. Illustration of the lateral shift of the chloride layers of FeOCl upon intercalation of TTF.

with respect to the other in order to accommodate the other sulfur in the same ring of TTF as the first (Fig. 2). The powder diffraction data can be fit best using a monoclinic cell with β = 115°, which is exactly the angle predicted if the TTF molecules are tilted at 25° from the perpendicular and dictate the relative orientation of the FeOCl layers. Since the TTF molecule spans two unit cells along a, it is not surprising that the a parameter of the intercalate must be doubled (vs. pristine FeOCl) to fit the data.

For both the TTT and TTN intercalates a slight variation of this model is necessary, due to the short S-S bonded distance (2.10Å)[10]. If one sulfur of the S-S pair rests in a hole formed by four chlorides, the bonded sulfur atom cannot occupy an adjacent hole along either a or c. Steric repulsions between host and intercalant are minimized if TTT and TTN orient themselves along the c axis, with the S---Cl repulsion again forcing a small elongation of the a axis. As a result, for TTT and TTN there are two angles of importance: θ = 42±5°, defined as the angle between the plane of the molecule and the b axis; and ϕ = 14±5°, defined as the angle between the S-S bond and the a - c plane (Fig. 1 (bottom)). With these values of θ and ϕ, it is not necessary for the chloride layers to shift with respect to one another to accommodate the intercalant, and the unit cell remains orthorhombic, as observed.

Based on this structural model, we can conclude that the intercalated organic molecules are in the correct relative orientation to achieve intermolecular π overlap, and possibly high conductivity, with the sulfur atoms in close contact with the chloride layers of FeOCl. Our model predicts a maximum stoichiometry of $FeOCl(TTF)_{1/8}$, and to date only $FeOCl(TTF)_{1/8.5}$ has been obtained.[11] The possibility of domains of intercalants within FeOCl, in which only the axes perpendicular to the layers are aligned, cannot be ruled out, however. Consequently, there may not be sufficient overlap of molecules within or between these domains for high conductivity. Neutron powder diffraction experiments on the TTF intercalate are in progress to further define the structure of the intercalant lattice, as are further synthetic endeavors with other host and guest molecules.

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