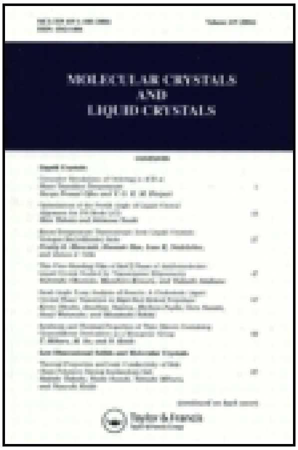

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Macroanionic Electron Acceptors for the Synthesis of Low-Dimensional Conductors: Intercalation of Tetraselenafulvalene and Tetramethyltetraselenafulvalene into Iron Oxychloride

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Macroanionic Electron Acceptors for the Synthesis of Low-Dimensional Conductors: Intercalation of Tetraselenafulvalene and Tetramethyltetraselenafulvalene into Iron Oxychloride

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Intercalation of the heteroaromatic π-donors tetraselenafulvalene (TSF) and tetramethyltetraselenafulvalene (TMTSF) into the layered host FeOCl results in new low-dimensional materials of stoichiometry $FeOCl(TSF)_{1/8.5}$ and $FeOCl(TMTSF)_{1/10}$. Powder x-ray diffracton data and FTIR spectra indicate that in each case the guest molecules are oriented perpendicular to the host layers and are present as the radical cations within the host galleries. Four-probe conductivity measurements show a 10^4 and 10^3-fold increase (for the TSF and TMTSF intercalates, respectively) in electrical conductivity over that of pristine FeOCl, although both $FeOCl(TSF)_{1/8.5}$ and $FeOCl(TMTSF)_{1/10}$ remain semiconductors.

INTRODUCTION

A number of synthetic strategies have been developed[1–14] to prepare organic metals and other low-dimensional conducting materials. These include electro-crystallization of electron donors and acceptors,[6–8] direct chemical reaction[9–12] and polymerization of metallomacrocycles and organic compounds.[13,14] Structural and electronic factors are crucial in determining the physical properties of the resulting products.[1–5] Two major requisites[1] for metallic conductivity in organic and organometallic low-dimensional materials are: i) crystallization in segregated stacks (or layers) of electron donors and acceptors; and ii) non-integral charge transfer between the stacks (i.e., partially filled conduction band).

To date, the electron acceptors utilized to prepare organic conductors include

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primarily organic π-acceptors and inorganic anions. Unfortunately, the molecular nature of these materials makes it impossible to ensure the formation of the segregated stack (e.g., TTF·TCNQ)[15] or corrugated layer [e.g., $(BEDT\text{-}TTF)_2I_3$][16] structures necessary to produce electrically conductive materials.[1] Consequently, a major, and as yet unmet, challenge for solid state chemists is to develop synthetic strategies which permit control of such structural features.

We are presently investigating the use of lamellar materials as macroanionic electron acceptors that provide a matrix that enforces a segregated stack structure upon organic π-donors. Chemical modification of the host or guest species can then be used to control the amount of charge transferred between donor and acceptor, since charge-transfer occurs in virtually all intercalation reactions.[17,18] Furthermore, the rigidity and non-molecular nature of the host materials may prevent structural instabilities leading to Peierls distortions and thus to insulating materials.

The synthetic method utilized is the intercalation of planar electron donors (or acceptors) into layered transition metal hosts. We have recently reported the intercalation of tetrathiafulvalene (TTF) and related tetrathiolenes[19] and of perylene[20] into the layered host FeOCl. The desired perpendicular host guest orientation[21] was observed for these materials, resulting in the formation of stacks of organic donors separated by FeOCl layers. Unfortunately however, the reactions were found to proceed with complete charge transfer[22,23] and, in the case of TTF, sulphur–sulphur contacts at distances greater than the sum of van der Waals radii[24] resulted in poor molecular overlap. Here, we report the synthesis and physical properties of $FeOCl(TSF)_{1/8.5}$ and $FeOCl(TMTSF)_{1/10}$. The selenium analogs of the TTF and TMTTF intercalates were investigated because: 1) They are poorer electron donors[25–27] than either TTF or TMTTF, and thus may provide partially oxidized guest stacks within the host galleries (requirement ii); and 2) The larger size of selenium vs. sulfur will result in greater molecular overlap between adjacent guest species.

EXPERIMENTAL

FeOCl was prepared[28] by reaction of Fe_2O_3 with a slight excess of $FeCl_3$ in an evacuated, sealed Pyrex tube for 1 week employing a temperature gradient of 370–340°C. The black-violet microcrystalline product was washed with acetone and dried in vacuo. The Fe:Cl ratio was checked by elemental analysis to assess the purity of the material. TMTSF was purchased from Strem Chemical Co. and purified by recrystallization from anhydrous toluene before use. TSF was prepared by modification of a procedure outlined by Cava *et al.*[29]; details of the synthesis will be published elsewhere. The intercalates were prepared by treating FeOCl with equimolar solutions of the appropriate tetraselenolene in anhydrous dimethoxyethane; 0.05 M TSF, 14–17d. at 70°C; 0.03 M TMTSF, 4 weeks at 85°C. The resulting black microcrystalline solids were then washed (DME, CH_2Cl_2) and dried in vacuo. All manipulations were performed under a dry nitrogen atmosphere. Elemental analyses (Fe, Cl, C, H and Se) are consistent with stoichiometries $FeOCl(TSF)_{1/8.5}$ and $FeOCl(TMTSF)_{1/10}$. Intercalation was confirmed for all materials by powder x-ray diffraction; the absence of the characteristic 7.917 Å interlayer reflection for pristine FeOCl[30] was used to verify complete intercalation.

A Guinier camera (Enraf Nonius model FR 552) equipped with a graphite monochromator to provide clean Cu $K\alpha_1$ radiation was employed to collect x-ray powder diffracton data photographically. The diffraction patterns were converted to 2θ and d using the least squares program PHOTO.[31] Cell parameters were obtained by indexing the powder patterns using a least squares program LATT[32] with FeOCl as a starting point. Fourier transform IR data were obtained on a Nicolet DX-5 spectrophotometer. Temperature dependent resistivity measurements were performed on rectangular specimens employing the standard dc four-probe technique with silver paint contacts to attach electrical leads. DC magnetic susceptibilities were measured with a squid magnetometer (S.H.E. model 905) over a temperature range of 6–300 K.

RESULTS AND DISCUSSION

FeOCl crystallizes in the orthorhombic space group Pmnm with a = 3.302Å, b = 3.780Å and c = 7.917Å. The FeOCl structure[30] consists of layers of distorted, edge-shared, $FeO_{4/4}Cl_{2/2}$ octahedra in which the Cl^- anions are cis-coordinated so that they are outermost on either side of the layers. Adjacent layers stack to form hexagonally close-packed (ABAB) sheets of chloride ions. Van der Waals attractions between adjacent layers result in relatively weak interlayer bonding interactions, which is manifested by the number and variety of intercalates known for FeOCl.[33,34]

The rate of intercalation into FeOCl is dependent upon the particle size of the host, solvent polarity, and the solubility and reduction potential of the guest species. Due to the poor solubility and relatively high reduction potential of TMTSF[26] (0.54 V vs. SCE), the rate of intercalation into FeOCl is slow. The reaction is also highly dependent upon solvent polarity, as reactions carried out using toluene or benzene as solvent failed. The reaction rate can be accelerated by using more polar solvents such as dimethoxyethane which appear to facilitate charge transfer, or by the use of ultrasound to reduce particle size prior to treatment with guest solutions.

The powder x-ray diffraction patterns of the intercalates were indexed using a body-centered unit cell, orthorhombic space group Immm or I222. The unit cell parameters are a = 3.786(5)Å, b = 3.323(2)Å, c = 26.98(3)Å; and a = 3.791(1)Å, b = 3.315(1)Å, c = 27.309(3)Å for $FeOCl(TSF)_{1/8.5}$ and $FeOCl(TMTSF)_{1/10}$, respectively. The structural and physical properties of the intercalates and FeOCl, for comparison, are summarized in Table I. Upon intercalation, the host undergoes an interlayer expansion (Δd) of 5.6Å for $FeOCl(TSF)_{1/8.5}$ and 5.9Å for $FeOCl(TMTSF)_{1/10}$, corresponding to the size of the guest species. These expansions are only 1.3Å less than the height of TSF and TMTSF (Figure 1), respectively, and are consistent with orientation of the planes of the guest molecules perpendicular to the host layers but slightly "nested" in the corrugated chloride layers of FeOCl. A slight interpenetration ($\approx$ 1Å) of the guest species into the host layers is typical for intercalation compounds of this type.[23] The organic donors are ap-

TABLE I

Structural and physical properties of FeOCl and the intercalates

Property	FeOCl	$FeOCl(TSF)_{1/8.5}$	$FeOCl(TMTSF)_{1/10}$
Interlayer distance (Å)	7.917	13.47	13.79
Interlayer expansion (Å)	—	5.6	5.9
Nesting (Å)	—	1.3	1.3
Charge transfer	—	≈1.0e^-	≈1.0e^-
σ_{RT} $(\Omega\text{-cm})^{-1}$	10^{-7}	5.0×10^{-3}	5.4×10^{-4}
Band gap (eV)	0.61	0.34	0.35

parently aligned with the molecular planes parallel to the *a*-axis; this has been confirmed for $FeOCl(TTF)_{1/8.5}$ by EXAFS[21] and neutron powder diffraction.[24] The intramolecular Se–Se distance of 3.4Å in TSF (Figure 1) fortuitously approximates the intralayer Cl–Cl distance along *a* (3.32Å) for FeOCl. The selenium atoms of the TSF (or TMTSF) molecules "nest" in a closest-packed manner in the corrugated chloride layers, thus locking the molecule in place along the *a*-axis. This is supported by the observed increase in the *a*-axis upon intercalation. This model places the TSF or TMTSF molecules in stacks along *b* at an intrastack distance of 3.79Å, which is within the sum of the van der Waals radii for Se (3.80[36]–4.00Å[37]). Typical Se–Se intra- and interstack distances[15,35] for conducting $(TMTSF)_2X$ salts (X = AsF_6^-, BF_4^-, BrO_4^-, ClO_4^- and PF_6^-) are between 3.7–4.0Å. This suggests that Se–Se overlap in $FeOCl(TSF)_{1/8.5}$ and $FeOCl(TMTSF)_{1/10}$ may be sufficient to result in formation of a band in the interlayer region. The perpendicular host–guest orientation is particularly surprising for the TMTSF intercalate, since its sulphur analog, TMTTF, is observed to intercalate with the plane of the TMTTF lying parallel to the FeOCl layers.[19] We believe this is due to the larger electronic radial distribution of the selenium atoms, resulting in enhanced molecular overlap between the guest molecules and the host and between adjacent guest molecules, thus stabilizing the perpendicular host–guest orientation.

The maximum stoichiometries calculated for perpendicularly oriented close-packed guest molecules are $FeOCl(TSF)_{1/8}$ and $FeOCl(TMTSF)_{1/8}$. Thus, in the case of FeOCl $(TSF)_{1/8.5}$, the guest molecules are very nearly close-packed within the interlayer gallery. The small difference in the observed and calculated stoichiometry may be due to vacancies within the interlamellar region or to small amounts (<3%) of unintercalated FeOCl undetectable by powder x-ray diffraction.

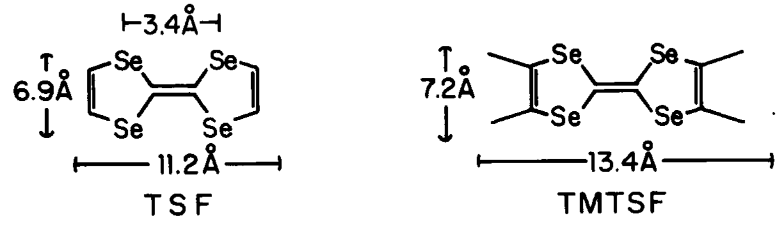

FIGURE 1 Schematic drawings of tetraselenafulvalene (TSF) and tetramethyltetraselenafulvalene (TMTSF) illustrating approximate dimensions.

An alternative structure is possible, in which the guest molecules form a double layer with their planes oriented parallel to the FeOCl layers. This model would, however, be expected to exhibit increased layer spacings of 7.8 and 8.8Å for the TSF and TMTSF intercalates, respectively and is inconsistent with experimental data.

The FTIR spectra of the intercalates are consistent with the presence of guest radical cations due to complete transfer of one electron per guest molecule to the FeOCl lattice. FeOCl(TMTSF)$_{1/10}$ shows a strong absorption at 1302 cm^{-1}, which has been assigned to the a_g ν_4 mode of the radical cation of TMTSF.[38] Similarly, FeOCl(TSF)$_{1/8.5}$ shows absorptions nearly identical to those of (TSF)ClO$_4$, with only small red shifts observed for some peaks. These data suggest that in each case the guests are present as the radical cation within the host lattice.

The resistivities of FeOCl(TSF)$_{1/8.5}$ and FeOCl(TMTSF)$_{1/10}$ are plotted as a function of temperature in Figure 2. The room temperature conductivities are $5.0 \times 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ and $5.4 \times 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for FeOCl(TSF)$_{1/8.5}$ and FeOCl(TMTSF)$_{1/10}$, respectively. These values represent a $10^3 - 10^4$ increase in conductivity over that of pristine FeOCl ($1 \times 10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$).[22] This increase is probably due to the electrons added to the host lattice upon oxidation of guest species; similar increases in conductivity are observed for nearly all intercalates of FeOCl.[33]

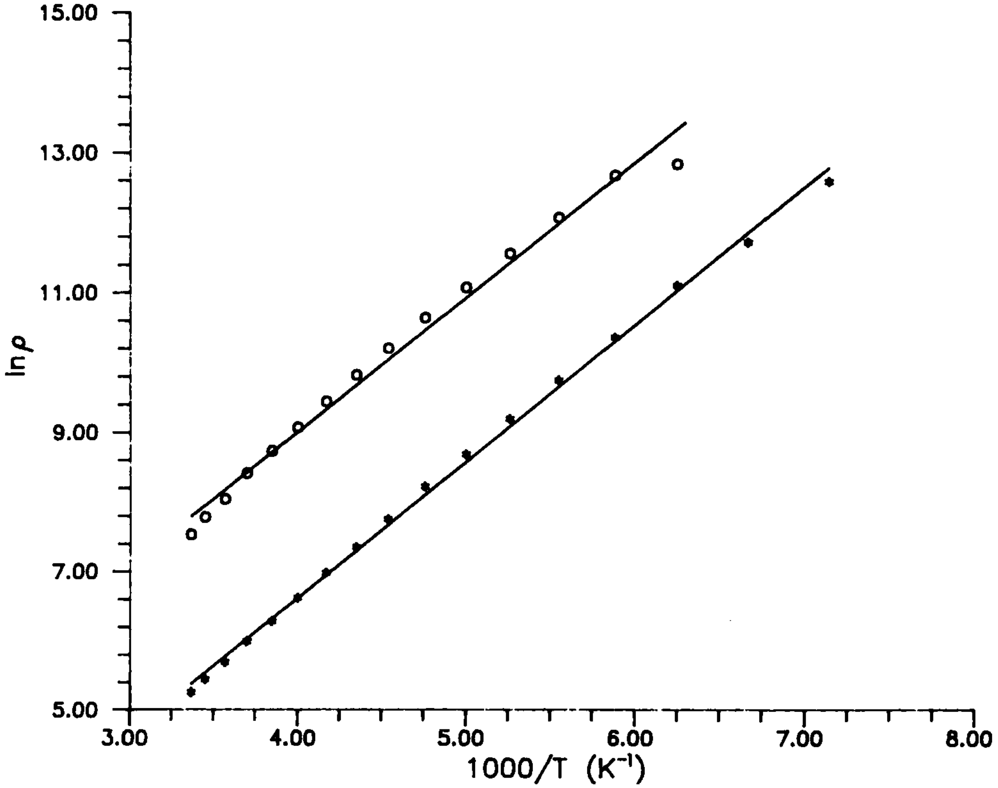

FIGURE 2 ln ρ Versus 1/T for FeOCl (TSF)$_{1/8.5}$ (stars) and FeOCl (TMTSF)$_{1/10}$ (open circles).

The x-ray powder diffraction data and close-packed calculations indicate that the TSF and TMTSF molecules are oriented perpendicular to the FeOCl layers and are stacked at short enough distances to result in appreciable orbital overlap between adjacent molecules. However, the FTIR data show that the guest species are completely oxidized to the radical cations. These results suggest that the molecular overlap within the donor stacks should make it possible to partially fill any potential conduction band by performing redox chemistry upon the guest molecules within the host galleries. Reduction of the donor stacks with cointercalation of alkali metals is currently being examined.

APPENDIX

TABLE SI

Powder pattern data for $FeOCl(TSF)_{1/8.5}$
$a = 3.786(5)Å$, $b = 3.323(2)Å$, $c = 26.98(3)Å$

h k l	$d_{obs}Å$	$d_{calc}Å$	I[a]
0 0 2	13.47	13.490	s
0 0 4	6.761	6.746	w
1 0 3	3.485	3.490	vs
1 0 5	3.101	3.099	vw
0 1 7	2.516	2.517	w
1 1 2	2.455	2.456	m
1 1 4	2.344	2.343	w
2 0 0	1.891	1.893	m
0 2 0	1.662	1.662	m
0 2 2	1.650	1.649	m
2 1 7	1.512	1.513	m
3 0 3 2 2 0	1.249	1.250	m
2 2 2	1.243	1.243	m

[a] Relative intensity.

TABLE SII

Powder pattern data for $FeOCl(TMTSF)_{1/10}$
$a = 3.791(1)Å$, $b = 3.315(1)Å$, $c = 27.309(3)Å$

h k l	$d_{obs}Å$	$d_{calc}Å$	I[a]
0 0 2	13.79	13.65	m
1 0 3	3.494	3.499	s
0 1 7	2.524	2.526	m
1 1 2	2.461	2.455	m
1 1 4	2.348	2.344	w
2 0 0	1.895	1.896	m
1 1 10	1.836	1.842	w
0 2 0	1.665	1.658	m
0 2 2	1.649	1.645	m
2 1 7	1.514	1.516	w
2 2 2	1.241	1.242	w

[a] Relative intensity.

TABLE III

Elemental analysis

			FeOCl(TSF)$_{1/8.5}$		
	%Fe	%Cl	%Se	%C	%H
Found	36.18	23.23	24.96	5.62	0.49
Calc.	36.14	22.94	24.64	5.62	0.31
			FeOCl(TMTSF)$_{1/10}$		
	%Fe	%Cl	%Se	%C	%H
Found	36.47	23.30	21.34	7.93	0.75
Calc.	36.72	23.31	20.78	7.90	0.79

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