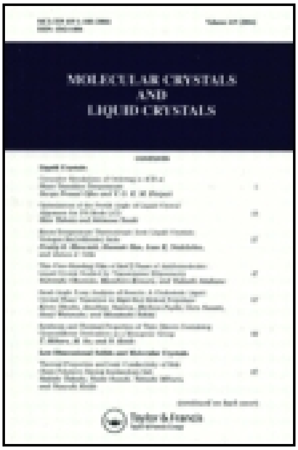

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# Structural and Physical Studies on a New Class of Low-Dimensional Conducting Material: Feoc1 Intercalated With TTF and Related Molecules

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# STRUCTURAL AND PHYSICAL STUDIES ON A NEW CLASS OF LOW-DIMENSIONAL CONDUCTING MATERIAL: FeOCl INTERCALATED WITH TTF AND RELATED MOLECULES

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Abstract Intercalation of TTF (tetrathiafulvalene), TTN (tetrathianaphthalene), and related organosulfur electron donors into FeOCl results in a significant expansion along the interlayer (b) axis, with the organosulfur molecules apparently inclined with respect to this axis. Electronic spectra suggest that the intercalates are semiconductors with band gaps of ca. 0.4 - 0.5 eV, consistent with previous conductivity data. Elastic neutron diffraction data (10K) show that magnetic ordering of the FeOCl host is abolished upon intercalation.

## INTRODUCTION

Intercalation chemistry of layered materials has been shown to be a promising approach to the synthesis of new low-dimensional materials with high electrical conductivity.[1,2] We report herein the results of structural and physical studies that extend our earlier work on organosulfur intercalates of FeOCl.[1-4]

## EXPERIMENTAL

Intercalates of FeOCl with TTF, TTN, TMTTF (tetramethyl-TTF), TTT (tetrathiatetracene), and DTT (dithiatetracene) were prepared by minor variations (time, temperature, solvent) of methods described previously.[1,2] Infrared, near infrared, and visible absorption spectra were measured on KBr pellets and Fluorolube mulls using Perkin Elmer 1430 and Cary 17 spectrophotometers. Neutron diffraction data were measured at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory, while X-ray absorption and X-ray powder diffraction data were measured and analyzed as described previously.[4]

## RESULTS AND DISCUSSION

### Structural studies

We have reexamined our EXAFS data, and find that the elongation along _a_ induced by intercalation is not as large as previously reported.[4] Lattice parameters of the intercalates are summarized in Table I. Inspection of Table I shows that slightly different phases of intercalates can be obtained using different solvents. A more detailed presentation of the structural results is in preparation.[5]

TABLE I Lattice parameters of intercalates.

| Material | $a^*$ | $b^+$ | $c^*$ |
|---|---|---|---|
| FeOCl | 3.78 | 7.92 | 3.30 |
| $FeOCl(TTF)_{0.12}$‡ | 3.78 | 12.83 | 3.33 |
| $FeOCl(TTF)_{0.11}(toluene)_{0.04}$ | 3.78 | 13.23 | 3.31 |
| $FeOCl(TTN)_{0.11}(toluene)_{0.05}$ | 3.80 | 15.43 | 3.34 |
| $FeOCl(TTT)_{0.14}$ | 3.80 | 15.45 | 3.34 |
| $FeOCl(TMTTF)_{0.08}$ | 3.80 | 11.32 | 3.32 |

*Å, from EXAFS data. +Å, from X-ray powder diffraction data.
‡from dimethoxyethane.

In order to ascertain whether the intercalants exhibit long-range order within the host, we have measured neutron diffraction data on FeOCl and the TTF and $d^4$-TTF intercalates ($d^4$-TTF was prepared as given in Ref. 6). No significant difference in the neutron diffraction data for the TTF and $d^4$-TTF intercalates was observed at 300 K, suggesting the absence of long-range ordering for TTF. We find that intercalation of TTF abolishes the magnetic ordering reported for FeOCl at low temperatures.[7,8]

## Physical studies

Since previous studies[1-3] have shown that the intercalants are best viewed as radical cations, this implies that an electron has been transferred to the FeOCl layers. X-ray near edge structure (XANES) spectra (data not shown) of FeOCl and $FeOCl(TTF)_{0.12}$ indicate a small but significant shift in edge position to lower energies for the intercalate, consistent with localized ferrous sites[9] due to donation of an electron from TTF.

A detailed comparison of the infrared spectra of FeOCl and $FeOCl(TTF)_{0.12}$ has allowed the bands due to $TTF^+$ to be assigned (Figure 1); the positions are very similar to those in the TTF-chloranil black crystalline phase, which consists of fully ionic

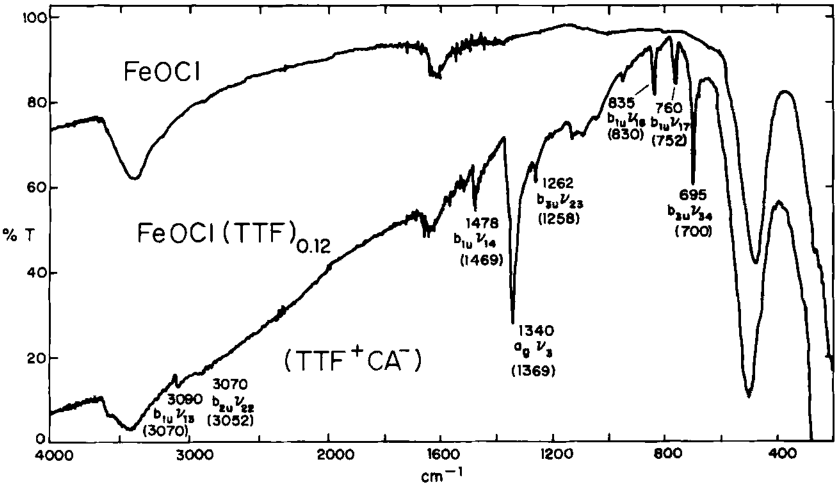

FIGURE 1 IR spectra of FeOCl and $FeOCl(TTF)_{0.12}$ (KBr pellets). Numbers in parentheses refer to TTF-chloranil salt $(TTF^+CA^-)$.[10]

segregated stacks of donors and acceptors.[10] The strong absorption at 1340 $cm^{-1}$ is attributed to $(TTF^{+})_2$ dimers. The visible absorption spectra[1] of $FeOCl(TTF)_{0.11}(toluene)_{0.04}$ suggests that these dimers are separated units, as in $(TTF)Br_{1.0}$.[11] The rising absorption between 1600 and 4000 $cm^{-1}$ suggests the presence of an electronic transition in this region. This is supported by absorption spectra measured from 350-2500 nm. These data indicate an absorption maximum at ca. 4000-2500 $cm^{-1}$ for $FeOCl(TTF)_{0.12}$, in agreement with the apparent band gap of 0.4 eV estimated from conductivity measurements (pressed powder).[2]

## ACKNOWLEDGEMENTS

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