Intercalation of Tetrathiafulvalene into Iron Oxychloride

By MARK R. ANTONIO and BRUCE A. AVERILL*
(*Department of Chemistry, Michigan State University, East Lansing,* MI 48824)

Summary Reaction of tetrathiafulvalene (TTF) in toluene with FeOCl yields the first intercalation compound containing TTF, with approximate stoicheiometry FeOCl-$[TTF]_{1/10}[C_7H_8]_{1/22}$; intercalation of TTF increases the electrical conductivity of FeOCl by *ca.* 10^2—10^3.

INTERCALATION of layered materials[1] such as FeOCl, the transition metal dichalcogenides (MY_2), and metal phosphorus trisulphides (MPS_3) is well established for polar organic compounds such as amines, amides, and phosphines,[2] and has recently been extended to include organometallic complexes such as cobaltocene.[3] We have been investigating the intercalation of redox-active guests into layered hosts, and have now extended the intercalation chemistry of FeOCl to include the organic electron donor tetrathiafulvalene (TTF). The intercalation of TTF is of special interest in light of the many organic charge-transfer salts of the TTF radical cation that exhibit high electrical conductivity, such as the prototypical 'organic metal,' TTF–TCNQ[4] (TCNQ = tetracyanoquinodimethane). As seen in the columnar stacking arrangement in TTF–TCNQ, which results in a highly anisotropic quasi-one-dimensional system, TTF has the potential to stack within the FeOCl layers, thus facilitating a facile charge-transfer between the guest donor and the host.

FeOCl was treated with toluene solutions of TTF in evacuated tubes at 60 °C for one week in the dark. The resulting black intercalate was washed with toluene and acetone, and dried *in vacuo*. Elemental analyses (Fe, Cl, C, H, S) are consistent with an approximate stoicheiometry of $FeOCl[TTF]_{1/10}[C_7H_8]_{1/22}$; preparations with a large FeOCl particle size ($\geqslant$ *ca.* 0·2 mm) result in a slightly lower TTF content and slightly higher toluene content.

The mass spectrum of the intercalate shows strong peaks due to toluene [*m/e* 91 (base peak), 92, 65, 63, and 39] and TTF[5] [*m/e* 204 (base peak), 159, 146, 102, 88, and 76]. Toluene deintercalates at lower temperatures (*ca.* 80—180 °C) than does TTF (*ca.* 200—375 °C), and can be selectively deintercalated by treatment at 100 °C and 10^{-2} Torr for 2—3 days, with no significant change in *X*-ray powder pattern or magnetic or electrical properties (*vide infra*).

X-Ray powder diffraction patterns of the intercalate exhibit new reflections. A strong low angle line at 13·60-(30) Å, with several higher order reflections, is observed; the characteristic 7·92 Å reflection[6] of pristine FeOCl is absent. The intralayer distance thus increases by *ca.* 5·7 Å upon intercalation. This expansion is approximately 1 Å less than the total van der Waals width of TTF (2·96 Å across S atoms in the same ring[7] plus 3·7 Å for two S van der Waals radii) and suggests a TTF orientation canted somewhat from the perpendicular to, and nested between, FeOCl layers.

I.r. and visible absorption spectra of the intercalate in KBr pellets indicate that TTF is oxidized to the radical cation, TTF^+, upon intercalation. The visible spectrum consists of continuously increasing absorption with decreasing wavelength, with a shoulder at 530 nm and broad 395 nm peak. These features correspond to the localized excitations of TTF^+ in the powder spectrum of $(TTF)Br_{1\cdot0}$.[8] The i.r. absorptions of the intercalated material occur at the following frequencies (cm^{-1}): 485(vs), 665(sh), 681(s), 740(m), 816(m), 1060(vw), 1250(w), 1332(vs), 1380(w), 1465(w), 1495(w), 1615(w, br), and 3070(vw). Except for the Fe–O stretch at 485 cm^{-1}, these modes closely correspond to the i.r.-active fundamentals and vibronic absorptions of the TTF radical cation,[8] with red shifts of *ca.* 10—12 cm^{-1} for most peaks; the toluene bands are not observed and may be obscured by the TTF^+ vibrations. From the stoicheiometry, the fraction of electrons donated by TTF (charge-transfer), presumably to FeOCl, is therefore *ca.* 0·1.

Zero-field ^{57}Fe Mössbauer measurements were performed at 4·2 K on FeOCl and on the intercalate. Intercalation of TTF significantly broadened the six-line spectrum of FeOCl; for example, the line widths at half-maximum for the highest velocity absorptions of FeOCl and the intercalate were 0·5 mm/sec and 0·8 mm/sec, respectively. In addition, a small amount ($\leqslant$ *ca.* 5%) of impurity iron (Fe_2O_3 from host decomposition[9]) with an effective field at the nucleus, H_{eff}, of *ca.* 530 kG, was observed. TTF intercalation causes no change in the isomer shift of FeOCl (δ +0·50 mm/sec relative to metallic Fe), and H_{eff} is essentially unchanged [FeOCl (432 kG) *vs.* the intercalate (430 kG)]. The principle component of the electric field gradient in the direction of H_{eff} is positive for both the intercalate and FeOCl. Most importantly, no evidence is observed for localized Fe^{2+} sites in the partially reduced FeOCl layers.

Room temperature magnetic susceptibility results, obtained with a Faraday balance, are $2{\cdot}7\mu_B$ for FeOCl and $2{\cdot}8\mu_B$ for the intercalate. The low effective moments (uncorrected) and their similarity are indicative of localized antiferromagnetic ordering.[10] The pressed pellet room temperature electrical conductivity of the microcrystalline intercalate ($8{\cdot}1 \times 10^{-4}$ to $3{\cdot}4 \times 10^{-3}$ $ohm^{-1}\,cm^{-1}$, depending on the preparation) is larger than that of FeOCl ($2{\cdot}7 \times 10^{-6}$ $ohm^{-1}\,cm^{-1}$) by *ca.* 10^2—10^3.

We thank T. A. Kent and E. Münck (Gray Freshwater Biological Institute, University of Minnesota) for the Mössbauer measurements and H. A. Eick (Michigan State University) for use of his *X*-ray diffraction instrumentation.

(*Received*, 27*th January* 1981; *Com.* 096.)

---

[1] 'Intercalated Layered Materials,' ed. F. A. Lévy, D. Reidel Publishing Co., Dordrecht, Holland, 1979; 'Proc. Int. Conf. on Layered Materials and Intercalates,' eds. C. F. van Bruggen, C. Haas, and H. W. Myron, The Netherlands, August 28—31, 1979, in *Physica*, 1980, **99** B + C, pp. 1—555.

[2] R. H. Herber and Y. Maeda, *Inorg. Chem.*, 1980, **19**, 3411; F. R. Gamble, J. H. Osiecki, M. Cais, R. Pisharody, F. J. DiSalvo, and T. H. Geballe, *Science*, 1971, **174**, 493.

[3] R. P. Clement, W. B. Davies, K. A. Ford, M. L. H. Green, and A. J. Jacobson, *Inorg. Chem.*, 1978, **17**, 2754; H. Schäfer-Stahl and R. Abele, *Mater. Res. Bull.*, 1980, **15**, 1157, and references therein; R. Clement and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1979, 1566.

[4] J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. Perlstein, *J. Am. Chem. Soc.*, 1973, **95**, 948.

[5] The mass spectrum of TTF^+ is identical with that of TTF°; F. Wudl, G. M. Smith, and E. J. Hufnagel, *Chem. Commun.*, 1970, 1453.

[6] M. D. Lind, *Acta Crystallogr., Sect. B*, 1970, **26**, 1058.

[7] W. F. Cooper, N. C. Kenny, J. W. Edmonds, A. Nagel, F. Wudl, and P. Coppens, *Chem. Commun.*, 1971, 889.

[8] R. Bozio, I. Zanon, A. Girlando, and C. Pecile, *J. Chem. Phys.*, 1979, **71**, 2282.

[9] H. Schäfer-Stahl, *Mater. Res. Bull.*, 1980, **15**, 1091.

[10] T. R. Halbert, D. C. Johnston, L. E. McCandlish, A. H. Thompson, J. C. Scanlon, and J. A. Dumesic, *Physica*, 1980, **99** B + C, 128.