An Aromatic Hydrocarbon Intercalate: $FeOCl(perylene)_{1/9}$

Joseph F. Bringley and Bruce A. Averill*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901, U.S.A.

Intercalation of the aromatic hydrocarbon perylene into the layered host FeOCl results in an approximately 10^5-fold increase in electrical conductivity; powder *X*-ray diffraction data and i.r. spectra indicate that the perylene guest is oriented perpendicular to the host layers and is present as the radical cation within the host galleries.

Organic metals[1] represent a class of materials in which segregated stacks of electron donors and acceptors are aligned in a parallel fashion with a non-integral degree of charge transfer occurring between the stacks. Electron donors utilized in organic metals to date include a variety of sulphur- and selenium-based heterocycles as well as arenes[2] such as perylene (Figure 1) and pyrene.

Much recent work in this area has focused on the design of new electron donors; in contrast, we are currently investigating the use of layered structures as macroanionic electron acceptors. To date, such work has been limited to the intercalation of TTF (tetrathiafulvalene) and other tetrathiolenes into the layered host FeOCl[3,4] and the intercalation of TTF into V_2O_5[5] and smectic clays.[6] We have now extended this approach to aromatic hydrocarbons, and report the first example of such an intercalate: $FeOCl(perylene)_{1/9}$.

The intercalate was prepared† by treating FeOCl with perylene (PE) in anhydrous dimethoxyethane (DME) to give a black microcrystalline solid that was washed with DME and acetone and dried *in vacuo*. Elemental analyses (Fe, Cl, C, H) are consistent with a stoicheiometry $FeOCl(PE)_{1/9}(DME)_{1/20}$. Intercalated perylene can be removed by prolonged extraction of the solid with polar solvents (*e.g.*, DME).

The mass spectrum of all samples showed peaks due to DME (*m/z* 91) and perylene (*m/z* 253). DME deintercalates at lower temperatures (*ca.* 160—200 °C) than does perylene (*ca.* 300—400 °C) and can be selectively deintercalated (190 °C, 10^{-2} torr, 2 days) with no significant structural or physical changes. The inclusion of solvent molecules within crystals of $(PE)_2X$ salts has been reported[7] previously.

The powder *X*-ray diffraction pattern of the intercalate was indexed using a body-centred unit cell with parameters a = 3.782, b = 33.372, and c = 3.318 Å. A strong low angle line at 16.56 Å is observed along with several higher order reflections. The absence of the characteristic 7.92 Å interlayer reflection for pristine FeOCl[8] was used to confirm complete

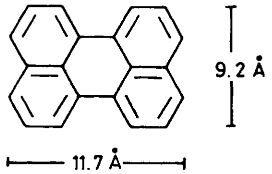

Figure 1. Schematic drawing of perylene illustrating approximate dimensions.

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† 0.1 M perylene, 21—30 days at 70—85 °C.

intercalation. The interlayer distance thus increases by approximately 8.6 Å upon intercalation.

This expansion is only 0.6 Å less than the height of the perylene (Figure 1), consistent with orientation of the perylene perpendicular to the host layers but slightly 'nested' in the corrugated chloride layers of FeOCl. An alternative possibility is a double layer of perylene molecules oriented parallel to the layers. The latter would, however, be expected to exhibit an increase in layer spacing of only 6.6—6.8 Å (twice the van der Waals thickness of an aromatic ring), which is substantially less than that observed. The former alternative is therefore more plausible, given the degree of nesting observed for many intercalates.[4] The maximum stoicheiometry calculated for close-packed perylene molecules is $FeOCl(PE)_{1/8}$ and $FeOCl(PE)_{1/8.5}$ for the perpendicular and parallel orientations, respectively, indicating that the intercalate contains very nearly close-packed perylene molecules.

The Fourier transform i.r. (F.t.i.r.) spectrum of $FeOCl(PE)_{1/9}(DME)_{1/20}$ shows strong absorptions.‡ The peaks not due to FeOCl are nearly identical to those in the F.t.i.r. spectrum of $(PE)_2{\cdot}3I_2$,[9] with only small red shifts observed for a few peaks. These data suggest that the intercalant is present as the perylene radical cation; the net charge transferred to the host is therefore 0.11 e^-/FeOCl.

Room temperature conductivities of pressed (300 atm) pellets of the microcrystalline intercalate ranged from 9.6×10^{-3} to 4.3×10^{-2} Ω^{-1} cm^{-1}, with an average value of 2.3×10^{-2} Ω^{-1} cm^{-1} for five preparations. This represents an increase in conductivity of about 10^5 over that of pristine FeOCl ($\sigma_{room\ temp.} = 10^{-7}$ Ω^{-1} cm^{-1}). Little can be concluded, however, regarding the origin of the increased conductivity, as similar increases are observed for nearly all intercalates of FeOCl.[10] The preparation and properties of related compounds are currently being examined, as are potential applications in heterogeneous catalysis owing to the presence of the guest radical cations.

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‡ ν[in cm^{-1} (relative intensity)]: 490 (vs), 696 (m), 819 (s), 1186 (s), 1348 (m), 1541 (s), 1631 (w, FeOCl), 2920 (w).

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