

Figure 3.—Nmr spectrum (60 MHz, *ca.* 35°) of $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$ in chloroform. Chemical shifts (in ppm relative to the $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$ methyl peak taken to be equal to -2.28 ppm from TMS from ref 11): a, -2.22 ; b, -2.28 ; a', -5.93 ; b', -6.23 . a and a' refer to the methyl and ring protons of $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$, and b and b' refer to the methyl and ring protons of $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$, respectively.

Further, no splitting or significant line broadening was observed at low temperatures (-60°).

The observation of a single methyl resonance signal for $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$ is consistent with a symmetrical structure, *i.e.*, a *trans* structure if, indeed, the complex is monomeric and nonionic. If the complex has a *cis* structure, one would expect to observe two methyl resonances since analogous *cis* tin and germanium complexes exhibit two methyl resonances near 35° .^{3b} Also at *ca.* 35° , *cis*-diacetoxybis(acetylacetonato)silicon(IV) has two acetylacetonate methyl resonances,²⁶ and tris(benzoylacetonato)silicon(IV) chloride exhibits three methyl resonances (indicating a *cis,trans* structure for the cation).^{3b} The above data make it unlikely that the observation of a single methyl resonance for $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$ is due to rapid exchange on the nmr time scale.

On the other hand, the position of the ring proton resonance signal (5.93 ppm) for $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$ is most consistent with an unsymmetrical complex. According to recent workers^{3b,11} acetylacetonate complexes having electrical asymmetry in the plane of the ring exhibit ring proton resonance signals which are significantly shifted relative to neutral and symmetrical complexes. Specifically for complexes of the type *cis*- $\text{M}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$ (M = group IV element) and for salts such as $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$ which ion pair to produce electrical asymmetry, the ring proton signals should occur from *ca.* 0.2 to 0.7 ppm downfield from the signals for the *trans* complexes. These recent observations suggest that $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$ is either ionic or unsymmetrical or both since the ring proton resonance signal is well into the region for unsymmetrical complexes. However, although the above correlation appears quite general for a number of representative acetylacetonates, it may be

that the silicon-acetylacetonate complexes are anomalous with respect to chemical shift data, and a *trans* monomeric and nonionic complex might also have a downfield ring proton signal. The supposition is supported by the fact that the chemical shift of the ring proton in *trans*-diacetoxybis(acetylacetonato)silicon(IV) is well into the region for unsymmetrical complexes.²⁶ Unfortunately, we have been unable to prepare other dihalobis(β -diketonate)silicon(IV) complexes which would provide further data to clarify existing uncertainties.

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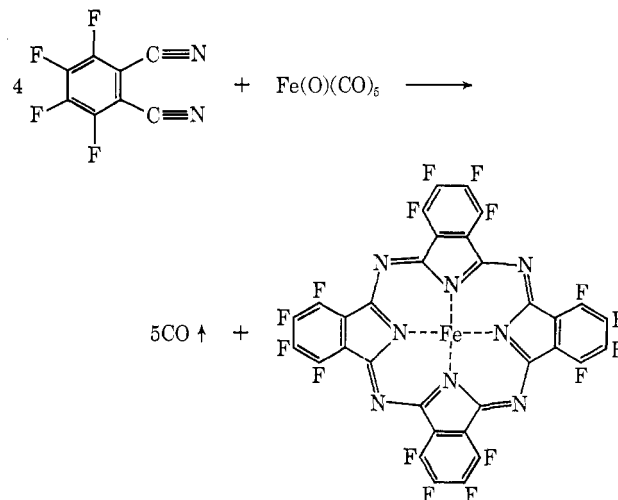
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A Fluorinated Iron Phthalocyanine

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We are currently studying the rates of reaction of ferrous phthalocyanine with bases, these displacing weaker bases from the axial sites at the ferrous center.¹ Solubility limitations are irksome in such systems, and one approach, to sulfonate the peripheral phenylene groups, gives a product which dissolves in water but is a ferric, not a ferrous, phthalocyanine in solution.² Our approach has been to prepare a ferrous phthalocyanine with all of the hydrogen atoms of the four peripheral phenylene groups replaced by fluorine atoms. This note gives details of the synthesis, which is by the method of Meloni, Ocone, and Block,³ and a preliminary account of some of the properties of this new compound.



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Experimental Section

A solution of iron pentacarbonyl (2.5 ml) (Alfa Inorganics) in 1-methylnaphthalene (50 ml) was slowly added in small portions over a period of 1 hr to a refluxing solution of tetrafluorophthalonitrile (Fluochem, Glossop, England) (12.5 g) in 150 ml of 1-methylnaphthalene. This was performed under an atmosphere of nitrogen; the solution became green-blue and a quantity of lustrous microcrystals was produced, after refluxing for 1 hr further.

After cooling, the mixture was diluted with 100 ml of benzene and filtered, and the solid was washed with the following solvents: benzene (five 60-ml portions) (dark washings), acetone (two 60-ml portions) (dark blue washings), and diethyl ether (50 ml) (blue washings); 8.6 g of a purple-blue microcrystalline powder resulted. It is soluble in simple alcohols, ketones, and donor solvents but insoluble in hydrocarbon solvents. Analysis gives good results for hexadecafluorophthalocyaninatoiron(II). *Anal.* Calcd for $\text{FeC}_{20}\text{F}_{16}\text{N}_8$: Fe, 6.52; C, 44.89; F, 35.50; N, 13.09. Found: Fe, 6.61; C, 44.80; F, 35.27; N, 12.92.

The infrared spectrum shows a series of very intense peaks reminiscent of ferrous phthalocyanine. The C-N stretch, at 1620 cm^{-1} , is much more intense than the corresponding one at 1610 cm^{-1} in ferrous phthalocyanine. Further assignments have not been made.

Properties.—Like ferrous phthalocyanine, it can be degraded with concentrated nitric acid to a phthalimide, in this case fully fluorinated. *Anal.* Calcd for $\text{C}_8\text{HF}_4\text{NO}_2$: C, 43.85; H, 0.46; F, 34.69; N, 6.9. Found: C, 43.68; H, 0.30; F, 34.95; N, 6.43. Boiling with concentrated aqueous ammonia, on the other hand, results in no adduct formation and no hydrolysis; N and F analytical figures and ir spectra of the fluorinated phthalocyanine are identical before and after boiling. Like ferrous phthalocyanine, it produces a green diamagnetic bis-pyridine adduct. *Anal.* Calcd for $\text{FeC}_{24}\text{H}_{10}\text{F}_{16}\text{N}_{10}$: Fe, 5.51; C, 49.73; H, 0.99; F, 29.97; N, 13.81. Found: Fe, 5.42; C, 49.68; H, 1.42; F, 29.90; N, 13.73. The ^{19}F nmr spectrum of this adduct in pyridine confirms its diamagnetism and structure, with just two ^{19}F environments ($\delta +126.5$ and 141.5 ppm as compared with tetrafluorophthalodinitrile with δ values of $+128.5$ and $+144.4$ ppm). (Small particles of "unpyridinated" iron complex, being paramagnetic, can "wash out" the nmr spectrum.)

A Perkin-Elmer Hitachi 124 vapor pressure machine was used to measure the molecular weight of a $6.2 \times 10^{-4} M$ solution of the fluorinated iron phthalocyanine, and this averaged at 905, as compared with a formula weight of 856. Thus acetone solutions are essentially monomeric at the concentrations used. Acetone solutions have a single broad peak in the visible spectrum, at 620 nm; accurate determination of the extinction coefficient was made difficult by "fading" which is being further investigated. Preliminary magnetic measurements on acetone solutions ($5 \times 10^{-3} M$) by Evans' method⁴ indicate paramagnetism, μ_{eff} at 33° being 3.3 ± 0.2 BM, which may be compared with a value of 3.0 ± 0.2 BM from preliminary measurements on the solid using a simple Gouy balance at 20° . These measurements tend to support a triplet ground state for iron in our fluorinated complex, confirming designation of the complex as an iron(II) compound.

In contrast to the measurements in acetone, a weak donor, measurements by Evans' method in dimethyl sulfoxide and pyridine solutions indicate diamagnetism for our complex, which would agree with it being low-spin iron(II) in an octahedral environment. The visible spectrum of such solutions is different from that of the acetone solutions; in dimethyl sulfoxide there are twin maxima of equal intensity at 630 and 660 nm; in pyridine there are virtually the same maxima, with a pronounced shoulder at 600 nm, too.

Preliminary kinetic measurements support the magnetic assignments; reaction of pyridine with our complex in acetone solution is slow, a spin change being involved; reaction in dimethyl

sulfoxide is much faster, no spin change being involved; these interesting reactions are being investigated more closely.

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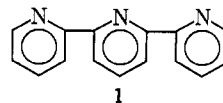
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Mono(2,2',2''-terpyridine) Complexes of Iron(II)

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The terdentate ligand 2,2',2''-terpyridine (terpy), 1,



is well known to form both mono and bis complexes³⁻⁹ with divalent transition metal ions. The bis complexes are presumed to have distorted octahedral structures. A single-crystal X-ray analysis has been carried out on $\text{Zn}(\text{terpy})\text{Cl}_2$ and the structure was shown^{10,11} to be five-coordinate. On the basis of a comparison of X-ray powder data it was suggested⁹ that the mono(terpyridine) chloride, bromide, and iodide of Zn(II), Co(II), Ni(II), and Mn(II) (and the bromide and iodide of Fe(II)) all have a five-coordinate structure similar to that of $\text{Zn}(\text{terpy})\text{Cl}_2$. The chloride of Fe(II) appears to be different. We have previously^{7,8} reported magnetic and spectral data on the Ni(II) and Co(II) systems. It is the purpose of this note to present data on a series of compounds having the empirical formula $\text{Fe}(\text{terpy})\text{X}_2$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{SCN}^-, 0.5\text{SO}_4^{2-}$).

Experimental Section

Preparations.—The substance having the empirical formula $\text{Fe}(\text{terpy})\text{Cl}_2$ was prepared by three methods. All gave the same product as evidenced by X-ray powder data. Method a was the procedure used by Broomhead and Dwyer.¹² In method b, 1.5 mmol of terpyridine and 1.9 mmol of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 30 ml of a 60:40 water-methanol solution. The solution was concentrated to a volume of 15 ml and 70 ml of acetone was added. A precipitate formed which was removed, washed with water, and dried under vacuum. Method c involved the heating

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