

Reaction of Carbazole Derivatives with Anhydrous Ferric Chloride (1)

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Sir:

The reaction of carbazole derivatives with anhydrous ferric chloride in organic solvents offers many interesting possibilities for analytical and synthetic studies with these heterocyclics. Intensely colored, stable complexes readily result from these reactions. Since the literature provides no previous reports on these reactions, the results of our preliminary studies in this area are now presented.

Carbazole and its alkyl derivatives react rapidly with ferric chloride in anhydrous benzene or 1,2-dichloroethane to yield bright-green complexes which convert slowly to a deep-blue color upon exposure to moisture. The reaction is exemplified by *N*-methylcarbazole. Figure 1 shows the

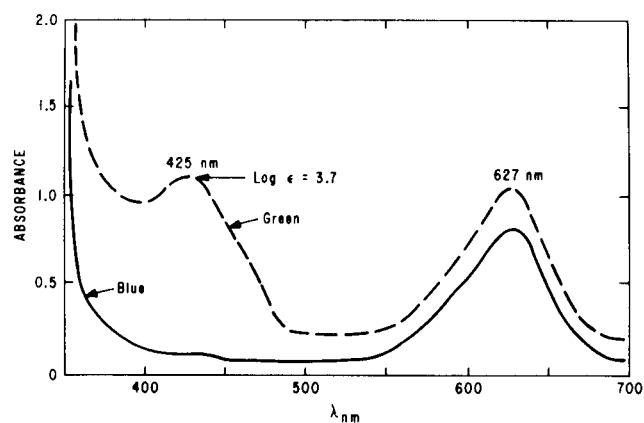


Figure 1. Visible Absorption Spectra of *N*-Methylcarbazole Fe_2Cl_6 Complexes.

visible spectrum of this anhydrous green complex and the hydrated blue complex which forms after exposure to a moist atmosphere. Due to the apparent insensitivity of the 627 nm band to hydration of the complex and to the slightly higher molar absorptivity of the 425 nm band in the anhydrous solution, the shorter wave-length was chosen for determining the composition of the complex by a method of continuous variation (Job's Method).

Crystals of anhydrous, sublimed ferric chloride are slightly soluble in 1,2-dichloroethane. A Beer's law curve was constructed (λ max 348 nm) assuming that the metal salt exists as the dimer Fe_2Cl_6 in this solvent (3).

The linearity of this plot at very low concentrations illustrated the nondissociation of the dimer in this solvent. The metal salt remains in the dimer form at low concentrations; so a Job's plot of the *N*-methylcarbazole complex was constructed by monitoring the complex at 425 nm as a function of the mole fraction ferric chloride dimer (Figure 2). The solid line shows excellent linearity at low mole

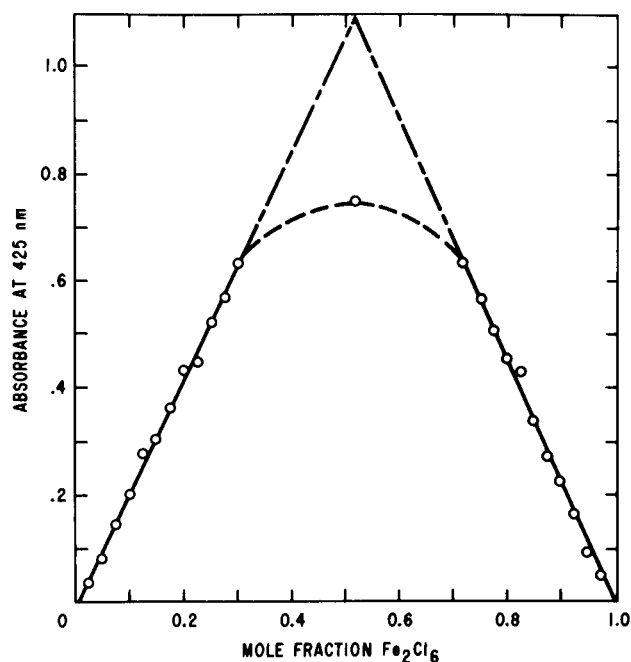


Figure 2. Job's Plot of *N*-Methylcarbazole Fe_2Cl_6 Complex.

fraction of either *N*-methylcarbazole or ferric chloride dimer; curvature with a single maximum at mole fraction 0.5 is observed at intermediate mole fractions. Extrapolation of the linear portions also intersects at 0.5. A composition of 1:1 for the complex is thus demonstrated by this technique. Elemental analyses of the solid green complex (crystallized from benzene) are also in accord with a 1:1 (or 1N:2Fe) complex. The elemental analyses of the solid complex show an N/Fe ratio of 0.123 (Theor. 1N/2Fe = 0.125) and an N/Cl ratio of 0.065 (Theor. 1N/

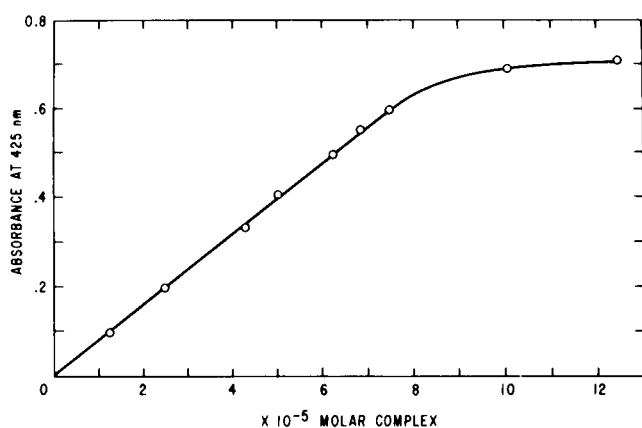


Figure 3. Beer's Law Behavior of *N*-Methylcarbazole Fe_2Cl_6 Complex.

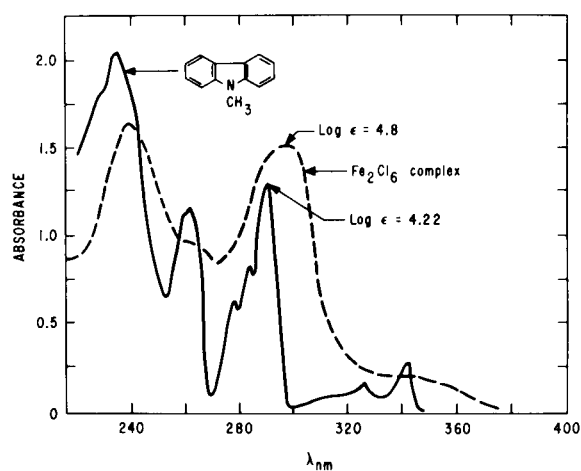


Figure 4. Comparison of Ultraviolet Spectra of *N*-Methylcarbazole and Its Fe_2Cl_6 Complex.

TABLE I
Visible Absorption Data for
Substituted Carbazole Fe_2Cl_6 Complexes

Compound	λ max complex
2-Methylcarbazole	400 nm
<i>N</i> -ethyl-3-acetylcarbazole	425
<i>N</i> -acetylcarbazole	450-500
1,2-Benzocarbazole	492
<i>N</i> -methyl-3-aminocarbazole	625

6Cl = 0.065). This evidence, therefore, suggests the formula $\text{C}_{13}\text{H}_{11}\text{NFe}_2\text{Cl}_6$ for the *N*-methylcarbazole complex in the solid state.

The 1:1 complex between *N*-methylcarbazole and ferric chloride dimer is high melting ($> 350^\circ$) and remarkably stable in anhydrous chlorinated solvents or in anhydrous atmosphere. Prolonged heating does alter the complex even though melting does not occur; elemental analyses after extended heating (100°) under vacuum show a slow loss of chlorine. A Beer's law plot (Figure 3) of the complex shows excellent linearity at low concentrations, demonstrating very little dissociation.

Figure 4 compares the electronic absorption spectra of *N*-methylcarbazole and its ferric chloride complex; at high dilution, the spectrum demonstrates that dissociation still has not occurred. The fine structure observed in the electronic absorption spectra of *N*-methylcarbazole is not seen after complexing with the ferric chloride dimer, implying that the complex molecule is nonplanar. The lone-pair electrons on the nitrogen are involved in the bonding with ferric chloride and are no longer available for conjugation with the π electrons of the fused benzo groups. The dominant features are two broad intense absorption bands at approximately 240 and 300 nm. The short wavelength band can reasonably be attributed to a π - π^* transition of the aromatic system in an *o*-*o'*-disubstituted biphenyl system (4). The high extinction coefficient ($\log \epsilon = 4.8$) of the long wavelength band implies another π - π^* transition. The lone-pair electrons on the heterocyclic nitrogen may be removed from the conjugated aromatic system by coordination with the metal in a manner not unlike that of α,β -unsaturated ketones (3).

Other types of carbazole derivatives have been qualitatively studied. These all react rapidly but not necessarily in a 1:1 ratio. The absorption maximum of the complex shifts with different substituents on the carbazole ring. Table I indicates this shift with representative substituents.

A very important property of these complexes is their rapid dissociation upon contact with a strong anion-exchange resin of the quaternary ammonium hydroxide type. This dissociation reaction (in 1,2-dichloroethane) enhances the analytical and synthetic usefulness of the complex because the original carbazole derivative remains in solution while ferric chloride is retained on the ion exchange resin. Thus, one is able to isolate and concentrate carbazoles by means of their ferric chloride complex, conduct reactions on the coordinated ligand, segregate the complex from non-reactive species, and recover the derivatives by means of anion-exchange resins (5). The complex reaction with ferric chloride is not selective to carbazoles when other nitrogen donors are present in a mixture; pyridines, phenazines, nitriles, and some amides also react. However, aromatic hydrocarbons, oxygen, and sulfur analogs of carbazoles do not form stable complexes under these conditions.

The properties of the alkylcarbazole-ferric chloride

complexes indicate that a strong bond exists between the lone pair of electrons on the heterocyclic nitrogen, which are essentially p in character, and the empty d -orbitals of the iron atoms in the Fe_2Cl_6 molecule (3); this complex should then be designated as an (n-d) type rather than a (π - π) type which is usually observed for many metal halides and aromatic hydrocarbons (6). Direct coordination of heterocyclic nitrogen to the metal halide could be considered a precursor to the actual transfer (oxidation) of the electron pair to the metal; a $2e$ transfer from carbazole to Fe(III) in acetonitrile has been demonstrated (7). The ease with which the heteroatom in carbazoles coordinates with the transition metal halide should be given serious consideration when attempting to predict orientations in reactions (*e.g.*, Friedel Crafts) with these heterocyclics.

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