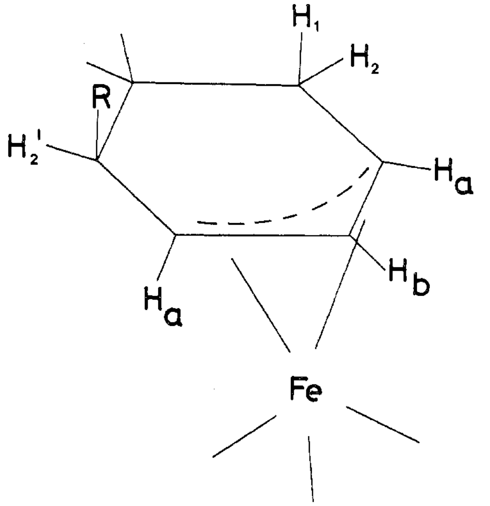

Figure 4. The coordinated allylic system.

count for the 9-G triplet if not also for the 26-G doublet (which could also be due to ^{31}P coupling).

One of the most likely modes of attack for the *n*-Bu radical on the cyclohexadiene ring is addition to the unsaturated system. This sort of attack at one of the unsaturated carbon atoms would probably occur from the side of the ring opposite to the metal atom, as has been observed repeatedly in such systems during nucleophilic attack on the ring.[3] If this were the case, the product would be the allylic radical shown in Figure 4.

The esr parameters to be expected from the allyl radical are 14 and 4 G for the five methylene and single methine protons, respectively.[4] The observed triplet splitting of 9 G is then assigned to the protons H_a, and this allows calculation of a spin density of ~65% in the allylic ring. Models indicate that the protons H_2 are very nearly in the plane of the allylic system, while proton H_1 (and the butyl group R) are *ca.* 90° out of this plane. As such, one expects the protons H_2 to be very weakly coupled to the allylic system, while H_1 would be strongly coupled with the unpaired spin. The maximum splitting from a proton such as H_1 under conditions of ideal geometry and unit spin density on the adjacent carbon is *ca.* 50 G.[5] Taking into account the spin density at the adjacent allylic carbon atom, the doublet splitting from H_1 should be 9 G/23 G × 50 G = 20 G, where 23 G is the splitting that H_a would cause if all the spin were localized on the one carbon atom.[6] This calculated value of 20 G is close to the doublet splitting of 26 G observed, and the increase can be accommodated if the allylic system has some cationic character.[7] Thus, for this model, the doublet splitting is assigned to a β proton rather than ^{31}P. This interpretation is also supported by the fact that the doublet hyperfine splitting is isotropic, which would be expected for a β-proton splitting, but not for a phosphorus splitting. Cationic character is expected if the metal acquires spin density by electron transfer from the allylic ligand.

Thus, on this hypothesis, the species observed has partial allyl radical character, but with considerable spin density on iron, and little, if any, on phosphorus. This excludes the participation of the d_{z^2} orbital, but suggests that there is bonding between the π_2 orbital of the allylic system and an orbital such as d_{xz} on iron. The very large g_1 value can then be understood if this is g_{zz}, since coupling between d_{xz} and d_{yz} is likely to be facile.

Another possible mode of radical attack, namely, hydrogen atom abstraction from the diene ring to give a coordinated cyclohexadienyl radical, must also be considered. This alternative, however, is less likely than that first discussed, as it would require that the hyperfine coupling from the CH_2 protons in the cyclohexadienyl radical be reduced from *ca.* 50 to *ca.* 9 G by delocalization onto iron. This implies that the 26-G doublet must arise only from ^{31}P. However, a phosphorus splitting should be anisotropic, as found for the anion, whereas in fact it is almost completely isotropic. On this basis, the former scheme involving radical attack at an unsaturated carbon atom is favored.

Registry No. $(C_6H_8)Fe(CO)_2PPh_3$, 12213-19-3; $[(C_6H_8)Fe(CO)_2(PPh_3)]^-$, 39797-00-7; *n*-butyl radical, 2492-36-6.

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Reactions of Octacyanomolybdate(IV). II. Coordination to Iron(III) and H$^+$ in Aqueous Solution

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The octacyanomolybdate(IV) ion generally forms insoluble complexes with divalent transition metal cations. However, if the transition metal cation is trivalent, formation of a soluble complex results on mixing aqueous solutions of each species.[1,2] Malik and Ali studied the reaction of Fe(III)[1] and Cr(III)[2] with the octacyanomolybdate(IV) ion in aqueous solution and found that, in both cases, soluble complexes are formed. Using Job plots, the complexes were shown to be stoichiometrically 1:1, *i.e.*, of composition, $M^{III}Mo(CN)_8^-$, where M^{III} is Fe(III) or Cr(III). A reexamination of the system in acid solution to avoid hydrolysis of Fe^{3+} and an attempt to isolate salts of $Fe\text{-}NCMo(CN)_7^-$ have been made.

Experimental Section

$K_4Mo(CN)_8\cdot 2H_2O$ was prepared by the method of Furman and Miller.[3] $Mo(CN)_8{}^{4-}$ solutions were stored in the dark for no more than 24 hr. Reagent grade $FeCl_3\cdot 6H_2O$ was used to prepare Fe(III) solutions. Suitable H^+ concentrations were maintained with standardized $HClO_4$. Ionic strength was maintained at 1.0 with $NaClO_4$ when $[H^+]$ was varied. Elemental analyses were performed by the Microanalytical Laboratory of the University of Illinois. All spectra were recorded, using a Cary 14 recording spectrophotometer.

Results and Discussion

Mixing aqueous solutions of *ca.* 5×10^{-3} *M* Fe(III) and $Mo(CN)_8{}^{4-}$ and 1 *M* H^+ changed the colors of the reagents from yellow to blue, indicating interaction between Fe(III)

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and $Mo(CN)_8^{4-}$. The blue complex exhibits a broad absorption band in the visible-near-infrared spectral region with a maximum at *ca.* 820 nm. This band was difficult to measure with precision. Signals exhibited considerable noise, and cyano complexes underwent photochemical decay at these wavelengths.

Composition of the Complex. The composition of the complex was determined by the method of continuous variations.[4] Acidic solutions (1 *M* H^+) whose total concentration of $Mo(CN)_8^{4-}$ and Fe(III) remained constant at *ca.* 5×10^{-3} *M*, but whose $[Mo(CN)_8^{4-}]/[Fe(III)]$ ratio varied, were prepared and the absorbances were measured between 650 and 900 nm. A plot of absorbance *vs.* the mole fraction of $Mo(CN)_8^{4-}$ present for each solution at a particular wavelength yielded curves with maxima at a mole fraction of $Mo(CN)_8^{4-}$ equal to 0.5. This behavior is indicative of 1:1 complex formation. The blue complex can be formulated as $FeMo(CN)_8^-$ formed according to the equation

$$Fe^{3+} + Mo(CN)_8^{4-} \overset{K_f}{\rightleftharpoons} FeMo(CN)_8^- \qquad (1)$$

The formation constant and molar absorptivity of the complex were estimated by the method of Drago and Rose[5] using eq 2, where K_f is the formation constant of the com-

$$K_f^{-1} = A/\epsilon_c - C_1 - C_2 + (C_1C_2/A)\epsilon_c \qquad (2)$$

plex, A is the absorbance of the complex at wavelength λ, ϵ_c is the molar absorptivity of the complex at λ, and C_1 and C_2 are the initial concentrations of the reactants. Absorbances for various Fe(III)-$Mo(CN)_8^{4-}$ reaction mixtures appear in Table I. For each set of data in Table I, the values of K_f^{-1} calculated were plotted on the same graph against the values of ϵ_c which were used to obtain them. Figure 1 shows the series of straight lines obtained, which intersected at a point giving ϵ_c and K_f^{-1} from which the formation constant of the complex was determined. Values of 90 ± 20 M^{-1} for the formation constant and 1700 ± 200 M^{-1} for the molar absorptivity of the complex at 820 nm were obtained. The relatively low value for the formation constant indicates a weak interaction between Fe(III) and $Mo(CN)_8^{4-}$. Malik and Ali,[1] working with neutral solutions, obtained a formation constant of *ca.* 10^4 M^{-1}. The discrepancy between their value and that obtained in this study prompted a study of the dependence of complex formation on the $[H^+]$ of the solution.

Dependence of the Formation of the Complex $FeMo(CN)_8^-$ on $[HClO_4]$. The effect of changing $[HClO_4]$ on the absorptivity of solutions ($[Fe(III)] = [Mo(CN)_8^{4-}] = 2.5 \times 10^{-3}$ *M*) and the formation constant of the complex is shown in Table II. It can be seen that as the $[HClO_4]$ of the reactant mixtures decreases, the formation constant for the complex increases, but that variation of $[H^+]$ at constant ionic strength has only a small, but opposite effect. The following equilibria may be considered as contributing to the observed effects

$$H^+ + Mo(CN)_8^{4-} \underset{}{\overset{1/K_{am}}{\rightleftharpoons}} HMo(CN)_8^{3-} \qquad (3)$$

$$Fe^{3+}(aq) + H_2O \overset{K_{af}}{\rightleftharpoons} Fe(OH)^{2+}(aq) + H^+ \qquad (4)$$

$$Fe^{3+}(aq) + ClO_4^- \overset{K_f'}{\rightleftharpoons} FeClO_4^{2+} \qquad (5)$$

Table I. Complex Absorbances in 1 *M* $HClO_4$

Plot of Figure 1	$10^3[Mo(CN)_8^{4-}]$, *M*	$10^3[Fe^{3+}]$, *M*	A(800 nm)
1	3.82	4.2	1.52
2	2.31	2.63	0.678
3	1.85	2.10	0.459
4	1.42	1.61	0.281
5	0.926	1.05	0.133
6	0.661	0.750	0.073

Table II. Dependency of K_{obsd} for the Complex $FeMo(CN)_8^-$ on $[HClO_4]$

$[HClO_4]$, *M*	A(800 nm)	K_{obsd},[b] M^{-1}	$A(\mu = 1.0)$
1.0	0.590[a]	76	0.590
0.5	0.810	116	0.580
0.1	1.300	254	0.530
0.05	1.450	315	0.515
0.01	1.557	350	0.470

[a] This is about 20% lower than that obtained from solutions used in Table I. Data obtained from particular stock solutions were self-consistent to within about 10%, while different preparations varied more. [b] Using 1700 for ϵ for the complex.

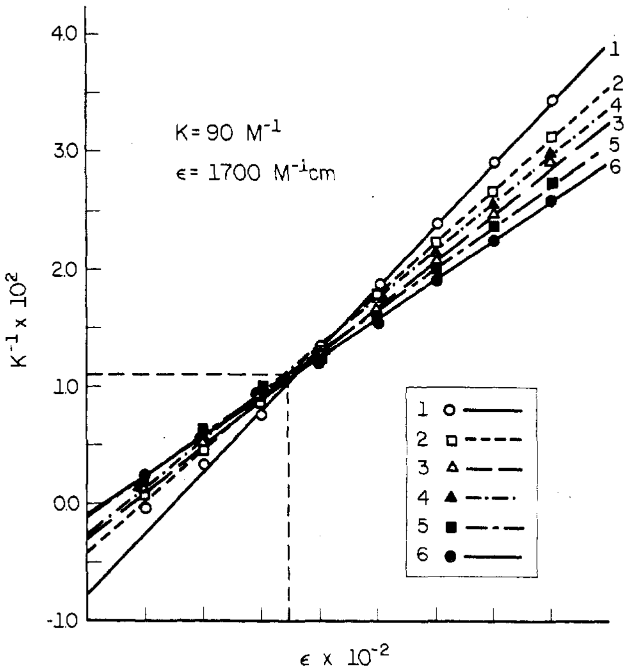

Figure 1. Plots used to determine the molar absorptivity, ϵ_c, and formation constant, *K*, of the complex formed between Fe(III) and $Mo(CN)_8^{4-}$.

The results at constant ionic strength are in accord with the conclusion that neither $FeOH^{2+}$ nor H^+ associates with $Mo(CN)_8^{4-}$. Formation of $FeOH^{2+}$ at low $[H^+]$ accounts for the small decrease in absorbance at $\mu = 1.0$. From the values of K_{obsd} calculated for systems with varying $[HClO_4]$, it is possible to approximate the values of K_f and K_f' using eq 6, where K_f is the formation constant for eq 1 and K_f'

$$1/K_{obsd} = \frac{1}{K_f} + \frac{K_f'[ClO_4^-]}{K_f} \qquad (6)$$

is the formation constant for eq 5. Figure 2 shows a plot of $1/K_{obsd}$ *vs.* $[ClO_4^-]$ giving a straight line with a slope equal to K_f'/K_f and an intercept equal to $1/K_f$. Analysis of Figure 2 yields values of 360 M^{-1} for K_f and 5.0 *M* for K_f', at 25°. The value of K_f for the formation of $FeMo(CN)_8^-$ is much lower than the value obtained by Malik and Ali[1] in neutral solutions. Why this is the case is unknown. No evidence from titrations, spectra, nor literature search for association of $Mo(CN)_8^{4-}$ with H^+ was found. Effects

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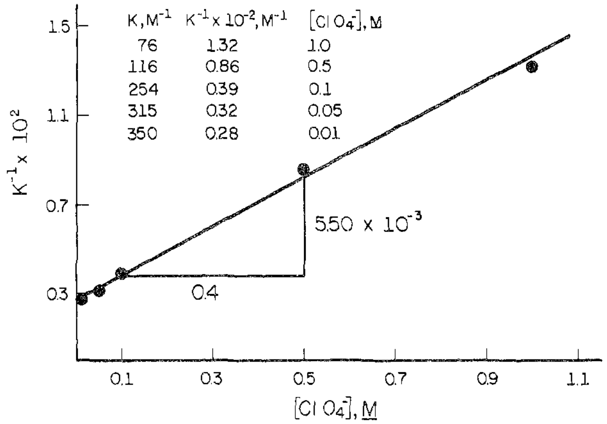

Figure 2. Plots of the reciprocal of the formation constant K *vs.* $[HClO_4] = \mu$.

attributed to K_f' may simply be ionic strength effects, but K_f' is very similar to values reported by Sykes[5a] at low ionic strength.

Ultraviolet Spectra. Yellow octacyanomolybdate(IV) ion exhibits general absorbance in the ultraviolet region of the spectrum, with a peak at 240 nm. This absorbance at the peak is lowered slightly by changing $[H^+]$ from 0.1 to 1.0 M at $\mu = 1.0$. The effect is barely enough to suggest a reaction between $Mo(CN)_8{}^{4-}$ and H^+, but not enough to use to measure an equilibrium constant. The uv absorbances of Fe(III) and Mo(IV) are too great to observe spectral changes at concentrations needed to produce significant formation of the blue complex. $Mo(CN)_8{}^{4-}$ is very susceptible to photochemical decomposition in the presence of either H^+ or Fe^{3+}.

The Insoluble Compound $Fe_4[Mo(CN)_8]_3 \cdot 12H_2O$. Various methods were used unsuccessfully in trying to isolate salts of the soluble complex $FeMo(CN)_8{}^-$ from solution. It appears that the interaction between Fe(III) and $Mo(CN)_8{}^{4-}$ is not sufficiently strong to allow isolation by the usual methods. Although the soluble complex could not be isolated from solution, mixing reactant solutions whose concentrations had been increased to 0.05 M produced an insoluble amorphous salt of composition $Fe_4[Mo(CN)_8]_3 \cdot 12H_2O$. On mixing the reactant solutions an immediate deep blue precipitate formed which was filtered, washed with water and acetone, and dried under vacuum. *Anal.* Calcd for $Fe_4[Mo(CN)_8]_3 \cdot 12H_2O$: C, 21.32; N, 24.87; H, 1.79; Fe, 16.53; Mo, 21.29. Found: C, 21.39; N, 24.50; H, 1.65; Fe, 16.17; Mo, 22.09. An infrared spectrum of the compound, as a Nujol mull, in the cyanide stretching region showed a broad absorption centering at 2135 cm^{-1} with weak shoulder bands at *ca.* 2160 and 2185 cm^{-1}. This spectrum differs greatly from the spectrum of the $K_4Mo(CN)_8 \cdot 2H_2O$ compound which consists of four sharp peaks at 2060, 2103, 2126, and 2136 cm^{-1}, with the main peak appearing at 2103 cm^{-1}. The broadening of the cyanide stretching bands and their shift to higher frequency are of interest in that they indicate bridging of the cyanide ligand as observed by Allen and Lippard[6] in $(UO_2)_2Mo(CN)_8 \cdot (6\text{-}8)H_2O$, by Shriver[7] in the adduct $K_4Mo(CN)_8 \cdot 8BF_3$, and by the present authors in divalent transition metal compounds of the $Mo(CN)_8{}^{4-}$ ion.[8] The same phenomenon is observed with heavy metal ferrocyanides[9] which are known to contain cyanide bridging ligands. Thus it appears likely that $Fe_4[Mo(CN)_8]_3 \cdot 12H_2O$ exists as an amorphous polymer containing bridging cyanide groups.

A halocarbon mull spectrum is very similar to the uv-visible spectrum in solution with the broad band in the near ir shifted to a maximum at 750 nm.

Bonding. Cyanide bridging ligands also can be postulated for the soluble complex $FeMo(CN)_8{}^-$. Precedence for such a conclusion can be found in observations of Haim and Wilmarth,[10] who proposed the existence of a cyanide bridge in the complex ion $[(NC)_5Fe^{II}CNCo^{III}(CN)_5]^{6-}$. Likewise, Burmeister and Sutherland[11] found that when $Co^{III}(NH_3)_5CN^{2+}$ reacts with $Co^{II}(CN)_5{}^{3-}$ to produce $Co^{III}(CN)_6{}^{3-}$, the sixth cyanide group of the product originates from the $Co^{III}(NH_3)_5CN^{2+}$ ion, which indicates that a bridging cyanide ligand occurs in the activated complex for the reaction. Similarly, Cr(III) is found bound to Fe(III) and Mo(V) by CN^- bridges following reduction of Cr(VI) by $Fe(CN)_6{}^{4-}$ [12] and $Mo(CN)_8{}^{4-}$.[13]

Bonding to nitrogen in $Mo(CN)_8{}^{4-}$ is seen to be very weak. No evidence of a protonated form has been found. Its association with triply charged Fe^{3+} is weak. However, it forms strong enough cyanide bridge bonds with metal ions in the solid state to give very insoluble polymers rather than crystalline arrays of simple discrete ions.[8] The blue complex is also produced when Fe^{2+} is mixed with $Mo(CN)_8{}^{3-}$. We are reminded of the $[FeFe(CN)_6{}^-]$ blue complex with mixed iron oxidation states; some delocalization of metal d electrons through the CN^- bridge is probably involved.

Registry No. $[FeMo(CN)_8]^-$, 39993-16-3; $Fe_4[Mo(CN)_8]_3$, 37359-93-6; $[Mo(CN)_8]^{4-}$, 17923-49-8.

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Nature of Iron(III) Chloride in Benzene

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During the investigation of the structure of the mixed dimer $[R_3NH^+Cl^-] \cdot [R_3NH^+FeCl_4{}^-]$ in benzene solution[1] differences in the infrared spectra were observed when anhydrous rather than hydrated iron(III) chloride was used in solution

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