deep-lying 4f orbitals are unaffected by the introduction of additional erbium ions into the crystal structure, and no interactions giving rise to ordering effects are observed.

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Dihalobis(triarylphosphine)iron(II) Complexes. Isotropic Proton Magnetic Resonance Shifts and the Kinetics of Ligand Exchange[1]

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A number of recent publications have dealt with the structure,[2] spectral and magnetic properties,[3,4] proton magnetic resonance spectra,[5-9] and ligand-exchange kinetics[10,11] of the pseudo-tetrahedral complexes of the type $M(TAP)_2X_2$, where TAP is triarylphosphine, M is Co(II) or Ni(II), and X is a halogen. We report here a study of the analogous iron(II) compounds. Complexes of this type were first reported by Naldini;[12] however, numerous synthetic attempts in two different laboratories failed to yield the desired compounds using her method. Instead they were prepared by a slight modification of the method by which Booth and Chatt[13] obtained bis(phosphine) complexes of iron(II) chloride.

Experimental Section

Dichlorobis(triphenylphosphine)iron(II).—Water was azeotropically distilled from 2.0 g of $FeCl_2 \cdot 4H_2O$ suspended in 100 ml of refluxing benzene under nitrogen for 24 hr. Triphenylphosphine (TPP) (5.0 g) was added and the mixture was refluxed for 6 hr. The solution was filtered hot under nitrogen and a few colorless crystals separated on cooling. The volume was then reduced to ~15 ml yielding additional product which was washed with benzene and ether under nitrogen. *Anal.* Calcd for $C_{36}H_{30}Cl_2FeP_2$: C, 66.40; H, 4.61; Cl, 10.89. Found: C, 65.92; H, 4.49; Cl, 11.02.

Dibromobis(triphenylphosphine)iron(II).—This light yellow compound was prepared by a method analogous to that of the chloride. *Anal.* Calcd for $C_{36}H_{30}Br_2FeP_2$: C, 58.43; H, 4.05; Br, 21.60. Found: C, 58.43; H, 4.05; Br, 21.36.

Diiodobis(triphenylphosphine)iron(II).—This was prepared analogously to the above compounds from hydrated iron(II) iodide prepared by dissolving iron metal in aqueous hydriodic acid, the excess water being removed under reduced pressure with heat. The azeotropic distillation of water from the benzene suspension was continued for 4 hr, and after addition of TPP an additional reflux period of 18 hr was allowed. The dark brownish black product was washed with benzene and ether under nitrogen. *Anal.* Calcd for $C_{36}H_{30}FeI_2P_2$: C, 51.84; H, 3.60; I, 30.43. Found: C, 51.82; H, 3.68; I, 30.35.

Dibromobis(tri-*p*-tolylphosphine)iron(II).—This was prepared in a manner analogous to $Fe(TPP)_2I_2$. The light yellowish product separated immediately and was washed with benzene and ether under nitrogen. *Anal.* Calcd for $C_{42}H_{42}Br_2FeP_2$: C, 61.23; H, 5.10. Found: C, 61.42; H, 5.22.

Proton Magnetic Resonance Spectra.—The pmr spectra were obtained using a Varian A-60-A instrument equipped with a variable-temperature probe. The spectra were calibrated using a wide-range oscillator and frequency counter to impress side bands of the internal standard, 1% TMS, onto the spectra. Samples were weighed out under nitrogen and dissolved in freshly dried (over molecular sieves) deuteriochloroform which had been deoxygenated in the usual manner.[11] The pmr sample tubes were sealed off *in vacuo* as described elsewhere.[11]

Electronic Spectrum.—The visible and near-infrared spectrum of $Fe(TPP)_2Br_2$ measured in chloroform solution in 1-cm cells on a Cary 14 instrument showed a broad band at 6410 cm^{-1} with ϵ_{max} 46 l. cm/mole. There were no other features except strong charge-transfer absorption in the ultraviolet region tailing into the visible region.

Magnetic Measurements.—The powder magnetic susceptibility of $Fe(TPP)_2Br_2$ was measured by the Gouy method at 24° using a diamagnetic correction of 418×10^{-6} cgs unit[3] yielding $\chi_M^{cor} = 11{,}530 \times 10^{-6}$ cgs unit and $\mu_{eff} = 5.25$ BM.

Results and Discussion

The pseudo-tetrahedral coordination of iron(II) in the bromide complex is supported by the measured magnetic moment which indicates a spin-free configuration and is in the range expected and generally found[14,15] for tetrahedrally coordinated iron(II). Further support for this structure comes from the "d-d" band at 6410 cm^{-1} which, considering the relatively high position of phosphine ligands in the spectrochemical series,[4] is expected in this region by comparison with the spectra[16] of a number of tetrahedrally coordinated iron(II) complexes with significant low-symmetry distortion.

Pmr Spectra.—Owing to the relative instability of the chloride and the insolubility of the iodide in suitable solvents, we have confined our magnetic resonance studies to the triphenylphosphine (TPP) and tri-*p*-tolylphosphine (TTP) complexes of iron(II) bromide. Unlike $Ni(TAP)_2Br_2$ and $Co(TAP)_2Br_2$ which show separate resonances for coordinated and uncoordinated ligand when both are present in chloroform solution at room temperature, complete averaging of the proton resonances of coordinated and uncoordinated TAP occurs for $Fe(TAP)_2Br_2$ at room temperature. Only at *ca.* −50° are separate resonances observable.

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Figure 1 shows the spectrum of $Fe(TTP)_2Br_2$ in the presence of an excess of uncoordinated phosphine under conditions of rapid ligand exchange. As with the cobalt(II) and nickel(II) analogs, the line widths increase in the order *para* < *meta* < *ortho* in the high-temperature region as expected for dipolar relaxation by the paramagnetic metal ion. Isotropic shifts may be obtained directly from a measurement of the low-temperature "frozen-out" resonances of the complex or from the completely averaged resonances at higher temperatures by making use of the equation

$$\Delta\nu_{\mathrm{obsd}} = P_{\mathrm{m}}\Delta\nu_{\mathrm{m}} \qquad (1)$$

$\Delta\nu_{\mathrm{obsd}}$ is the averaged resonance position relative to the diamagnetic resonance, $\Delta\nu_{\mathrm{m}}$ is the isotropic shift of the complex proton at the temperature of the measurement, and P_{m} is the mole ratio of coordinated ligand to total ligand. Table I presents the isotropic shifts for the coordinated triarylphosphine at 25°. The data for the cobalt(II) and nickel(II) complexes[17] are presented for comparison.

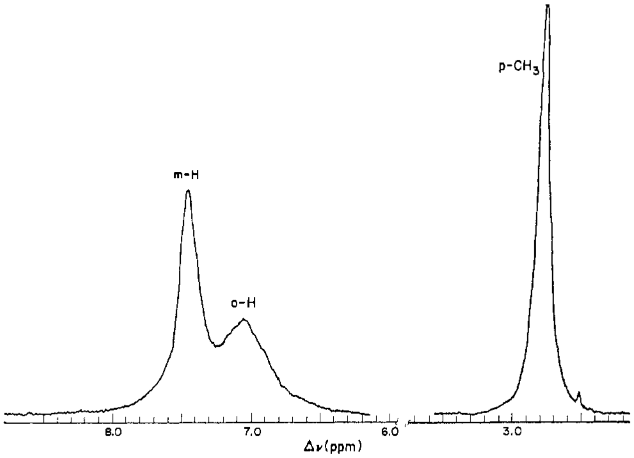

Figure 1.—Proton magnetic resonance spectrum of 0.0152 *M* $Fe(TTP)_2Br_2$ with 0.636 *M* (TTP) in deuteriochloroform solution at 33°, referenced to TMS.

TABLE I

ISOTROPIC PROTON RESONANCE SHIFTS[a] AND RATIOS FOR $M(TPP)_2Br_2$ AND $M(TTP)_2Br_2$ AT 25°[b]

Complex	*ortho*	*meta*	*para*[c]	*para*/ *ortho*	*meta*/ *ortho*	*para*/ *meta*
$Fe(TPP)_2Br_2$	5.33	−6.38	8.42	1.58	−1.20	−1.32
$Co(TPP)_2Br_2$	10.50	−8.50	11.75	1.12	−0.81	−1.38
$Ni(TPP)_2Br_2$	8.42	−11.00	13.00	1.54	−1.31	−1.18
$Fe(TTP)_2Br_2$	4.58	−6.25	−8.75	−1.91	−1.36	1.40
$Co(TTP)_2Br_2$	10.15	−8.72	−12.65	−1.25	−0.86	1.45
$Ni(TTP)_2Br_2$	9.13	−11.87	−15.15	−1.66	−1.30	1.28

[a] In ppm from the diamagnetic resonance position. [b] TPP = triphenylphosphine, TTP = tri-*p*-tolylphosphine. Cobalt and nickel data from ref 17. [c] *para* refers to *p*-H(TPP) or *p*-CH_3-(TTP).

The signs of the isotropic shifts for the present iron complexes are indicative of π-type spin delocalization in the ligand aryl groups as was found[17] in the cobalt and nickel complexes of this type. This suggests that the Fermi contact-shift mechanism dominates any dipolar (pseudo-contact) shifts which may be present. However, the isotropic shift ratios (Table I) differ from those of either the cobalt or nickel complexes, implying that a dipolar contribution to the total shifts is present. In view of the number of unknown parameters and assumptions involved in an analysis[17] of this effect, no quantitative treatment along these lines has been attempted. The magnitudes of the isotropic shifts at given temperatures are proportional to $S(S+1)$ and for the present iron complexes ($S = 2$) are somewhat less than those of the cobalt ($S = {}^3/_2$) and nickel ($S = 1$) analogs[17] indicating a considerably smaller degree of spin delocalization. Thus the degree of spin delocalization increases in the order Fe < Co < Ni.

Kinetics of Ligand Exchange.—Kinetic parameters for the TPP complexes were obtained by standard line-width techniques[18,19] employing the averaged *meta* proton resonance of the complex[19] while shift techniques[19] were applied to the *p*-tolylmethyl resonance data in the region of intermediate exchange for the TTP complexes. The average residence time of a ligand on the complex, τ_{m}, was computed in each case as a function of temperature for several concentrations of excess ligand. The pertinent data and results are summarized in Table II.

TABLE II

LINE-WIDTH DATA AND KINETIC PARAMETERS FOR $Fe(TPP)_2Br_2$ AND $Fe(TTP)_2Br_2$

Temp, °C	$(\Delta\nu^1/_2)_{\mathrm{cor}}$,[a] cps	$\Delta\nu_{\mathrm{m}}$,[b] cps	$10^4\tau_{\mathrm{m}}$,[c] sec
$Fe(TPP)_2Br_2$, [TPP] = 0.12 *M*, P_{m} = 0.432			
−28.0	196	466	1.66
−16.5	130	445	1.26
−3.0	84	422	0.87
+8.5	54	405	0.61
[TPP] = 0.17 *M*, P_{m} = 0.398			
−28.0	132	466	1.21
−16.5	104	445	1.05
−3.0	56	422	0.63
+8.5	40	405	0.45

Temp, °C	$\Delta\nu$,[d] cps	$10^4\tau_{\mathrm{m}}$, sec
$Fe(TTP)_2Br_2$, [TTP] = 0.85 *M*, P_{m} = 0.0342		
−43.0	9.4	2.55
−39.0	15.0	1.54
−30.0	18.0	1.11
−20.0	21.0	0.52
[TTP] = 0.64 *M*, P_{m} = 0.0456		
−43.0	11.6	2.73
−39.0	16.0	2.04
−30.0	22.0	1.34
−20.0	24.6	1.01

[a] Peak width at half-height of averaged *meta* resonance corrected for diamagnetic peak width. At the temperature of these measurements there is essentially no overlap between the *meta* and *ortho* resonances. [b] Isotropic shift of *meta* resonance from diamagnetic position of protons of TPP (−432 cps from TMS): G. Shaw, J. K. Becconsall, R. M. Canadine, and R. Murray, *Chem. Commun.*, 425 (1966). [c] $\tau_{\mathrm{m}} = \pi(\Delta\nu_{1/2})_{\mathrm{cor}}/P_{\mathrm{m}}(\Delta\nu_{\mathrm{m}})^2$. [d] Shift of *p*-$CH_3$ resonance from diamagnetic position (−143 cps from TMS).

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In each case the exchange kinetics is second order as was observed with the analogous Co(II) and Ni(II) systems.[10 11] For second-order kinetics $1/\tau_m = k_2 \cdot$ [ligand] and $k_2 = (kT/h)\exp[(\Delta S^{\ddagger}/R) - (\Delta H^{\ddagger}/RT)]$. Table III gives the resulting kinetic parameters obtained from a plot of log (k_2/T) *vs.* $1/T$ along with the corresponding Ni(II) and Co(II) values for comparison.[11]

TABLE III

KINETIC PARAMETERS FOR LIGAND EXCHANGE WITH ML_2X_2

Complex	$k_2(25°)$ ($\pm 0.5 \times 10^n$)	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
L = TPP			
$FeBr_2$	2.0×10^5	3.8 ± 0.5	-22 ± 3
$NiBr_2$	6.9×10^3	4.7 ± 0.4	-25 ± 2
$CoBr_2$	8.7×10^2	7.7 ± 0.5	-19 ± 3
L = TTP			
$FeBr_2$	6.3×10^5	4.0 ± 0.8	-19 ± 5
$NiBr_2$	6.1×10^3	5.2 ± 0.8	-24 ± 4
$CoBr_2$	1.8×10^3	5.5 ± 0.9	-25 ± 4

The results are consistent with an associative mechanism involving a five-coordinate transition state. The trend in lability, Fe > Ni > Co, is apparent (particularly from the more accurate TPP data) and seems to be mainly an enthalpy of activation effect. Ligand field arguments predict that the tetrahedral d^6 ground state will be stabilized to a lesser extent than that of the d^7 and d^8 analogs; this is consistent with the observed greater lability of the iron complexes. On the other hand, the same simple electrostatic model suggests that a pentacoordinate transition state of d^6 will be less stable than of the d^7 and d^8 counterparts, which would predict an order of lability Co, Ni > Fe. Clearly these models are too crude to allow a realistic assessment of the relatively delicate energy balance which governs these ligand-exchange reactions. Nevertheless it seems apparent that d-electron effects are important in determining relative rates in reactions of this type.

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Mechanism of the Ferricyanide Oxidation of Thiols[1]

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There have been relatively few investigations of the mechanism of the oxidation of organic substrates by ferricyanide. However, since these oxidations are almost universally base catalyzed, it seems attractive to suggest that the reactions generally involve electron abstraction by ferricyanide from an anion derived from the substrate. Recently, however, Kolthoff and coworkers[3] have suggested that the oxidation of thiols proceeds *via* a different path. We now wish to report a reinvestigation of this reaction.

In the previous work, *n*-octanethiol was found to be oxidized to the corresponding disulfide in aqueous acetone with the rate law being

$$v = k[RSH][HO^-][Fe(CN)_6{}^{3-}]$$

Of particular significance was the rate depression observed on addition of potassium cyanide. Using equimolar amounts of thiol and ferricyanide (7.25×10^{-4} *M*) a linear decrease in rate constant with increase in cyanide concentration was noted until at about 4×10^{-4} *M* KCN the rate became almost independent of the cyanide concentration.

On the basis of these observations, the mechanism below was proposed

$$RSH + HO^- \rightleftharpoons RS^- + H_2O \quad \text{(fast)} \qquad (1)$$

$$RS^- + Fe(CN)_6{}^{3-} \rightleftharpoons RSFe(CN)_5{}^{3-} + CN^- \quad \text{(fast)} \qquad (2)$$

$$RSFe(CN)_5{}^{3-} \longrightarrow RS\cdot + Fe(CN)_5{}^{3-} \quad \text{(slow)} \qquad (3)$$

$$Fe(CN)_5{}^{3-} + CN^- \longrightarrow Fe(CN)_6{}^{4-} \quad \text{(fast)} \qquad (4)$$

$$2RS\cdot \longrightarrow RSSR \quad \text{(fast)} \qquad (5)$$

This scheme will explain the rate depression observed since cyanide ion will repress equilibrium 2. Presumably some other process must also be available to account for the small rate of oxidation in the presence of excess cyanide ion.

Although this scheme will account for the results, step 2 is surprising since cyanide ion itself will not exchange with ferricyanide[4] under the conditions of the experiment. One may wonder why the mercaptide ion would be so much more effective than the cyanide ion. We have tested the mechanism by carrying out the reaction in the presence of cyanide-C^{14}. Here, we would expect a facile induced exchange resulting from reactions 2 and 4. The potassium ferrocyanide isolated after essentially complete reaction showed less than 0.1% exchange. The absence of exchange indicates that the above mechanism cannot be correct.

It is clear that cyanide ion cannot interact with ferricyanide in such a way as to reduce its reactivity. However, it would not be unreasonable to expect the thiol to react with cyanide. The reaction of hydrogen sulfide with nitriles is known to be a facile reaction.[5] This possibility was examined. The Raman spectrum of potassium cyanide in 60% aqueous acetone containing a pH 11.3 carbonate–bicarbonate buffer had a $C\equiv N$ band at 2086 cm^{-1}.[6] The addition of 1 equiv of 2-hydroxyethanethiol (*n*-octanethiol could not be used because of its low solubility) decreased the band

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