centrations) with respect to hydroxide ion. A similar mechanism to that suggested for the formation of NiApSo is thus indicated for the formation of the intermediate. By working at high [OH⁻], k_1 has been determined, (2.44 ± 0.2) $\times 10^{-2} M^{-1}$ min⁻¹. Again no spectral changes from the starting material are detected at zero time and thus K for the adduct has not been determined. For the second stage, the rate of formation of the macrocycle is dependent on [intermediate] and on hydroxide ion as before. For this stage, k_1 (corresponding to the formation of an adduct involving the unreacted end of the ethylenediamine molecule in the intermediate) is $\sim 1.3 \times 10^{-2}$ min⁻¹.

Further work is planned in this area to obtain complete kinetics data over a range of temperatures and to obtain more information relevant to the mechanisms proposed above. It is anticipated that a knowledge of the mechanisms of formation of macrocyclic complexes should lead to a more complete understanding of the factors controlling their formation and should also lead to the development of new and improved syntheses.

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High-Spin Iron(III) Tetraphenylporphine with Unusually Large Rhombic Character

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The EPR spectrum of the high-spin heme Fe(III) in cytochrome P-450 from various sources shows a characteristic absorption with g values near 8, 3.7, and 1.7, indicating that the heme iron site has an unusually high rhombicity.[1-7] This is in contrast with the situation found in numerous other ferric heme proteins in which the crystal field symmetry around the metal ion is axial or nearly axial[8] as demonstrated by EPR absorptions with $g = 6$ and 2. No explanation has yet been presented as to the origin of such unusual distortion in P-450. One of the questions to be asked may be whether or not such a highly rhombic field can be simulated outside the biological milieu, using some model heme compound. We have undertaken such studies using an iron(III)–tetraphenylporphine complex (TPPFe^{III}X, where X means an anion) with a wide variety of nitrogen- and sulfur-containing ligands in several organic solvents at and below 77°K. However, none of these systems so far investigated as a frozen solution displayed more than a slight splitting or broadening in the $g = 6$ EPR absorption ($\Delta g_\perp \leq 0.6$).

We have found, however, that EPR absorptions corresponding to the structures with various degrees of large rhombicity can be observed when TPPFe^{III}X is coprecipitated with an excess of free TPPH$_2$. The highest rhombicity observed in this model system is indeed large enough to be compared with the values in cytochrome P-450. Although this
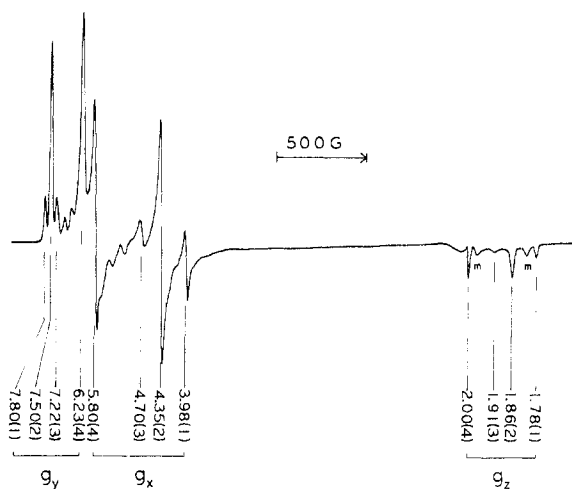

Figure 1. EPR spectrum of the ferric high-spin TPPH$_2$(FeCl), the mixed crystalline precipitate of TPPFe^{III}Cl and free TPPH$_2$, obtained from acetone and observed at 8°K. The effective g values are indicated for the four species. The peaks designated "m" are tentatively assigned to the transition in the middle Kramers doublet.[18]

model system undoubtedly satisfies only some of the conditions for realizing the extreme distortion in P-450 and, therefore, may not be a model for P-450, we present in this note the account in some detail with the hope of stimulating further studies on the subject.

Materials and Procedures

TPPFe^{III}Cl was synthesized in dimethylformamide[9] and purified by a dry Al$_2$O$_3$ column. Anal. Calcd: C, 75.06; H, 4.01; N, 7.96; Cl, 5.03. Found: C, 75.22; H, 4.01; N, 8.25; Cl, 5.14. TPPFe^{III}CH$_3$COO was prepared in a chloroform–acetic acid mixture and was converted to TPPFe^{III}F by ligand exchange.[10]

A chloroform solution of TPPFe^{III}X and TPPH$_2$ (w/w = 1/100) was poured into a large volume of polar solvent such as acetone, methanol, acetonitrile, or DMSO. Elemental analysis of the crystalline precipitate showed the actual [Fe]:[TPP] ratio to be 1:250 or less. EPR spectra of the resulting crystalline precipitate, TPPH$_2$(FeX)[11], after filtering and drying, were taken by using a Varian V4502 spectrometer with 100-kHz field modulation. The temperature was held constant between 5 and 10°K with an Air Products Heli-tran variable-temperature system.

Results and Discussion

In Figure 1 is shown a typical EPR spectrum, which can be interpreted as resulting from several distinct species of high-spin TPPFe^{III} complexes with different degrees of rhombicity. In fact, the effective g values determined from the spectra can be well fitted to the equations[12,13]

$$H = D(S_z^2 - S(S + 1)/3) + E(S_x^2 - S_y^2) + 2.0023\beta H \cdot S$$

$$g_{x,y} = 6.01 \mp 24(E/D) - 18.7(E/D)^2$$

$$g_z = 2.00 - 33.8(E/D)^2$$

Thus we are dealing with only the lowest Kramers doublet. The E/D value thus determined varies from 0.008 to 0.08 and the percentage rhombicity,[8] $R = (\Delta g/16) \times 100$, is 2%–24%. The maximum rhombicity observed in the model system is indeed almost the same as in P-450.

Among the component peaks, the one representing the species with the highest distortion ($g = 7.80, 3.98, 1.78$) is of particular interest in that the spectral position is unaffected by the solvent from which the crystalline precipitate is formed. In contrast, the number of the *less distorted* species and their g values are dependent upon whether the solvent used was acetone, methanol, DMSO, or acetonitrile. This observation implies that the solvent molecules are not associated with the rhombic environment of the most distorted species, but they
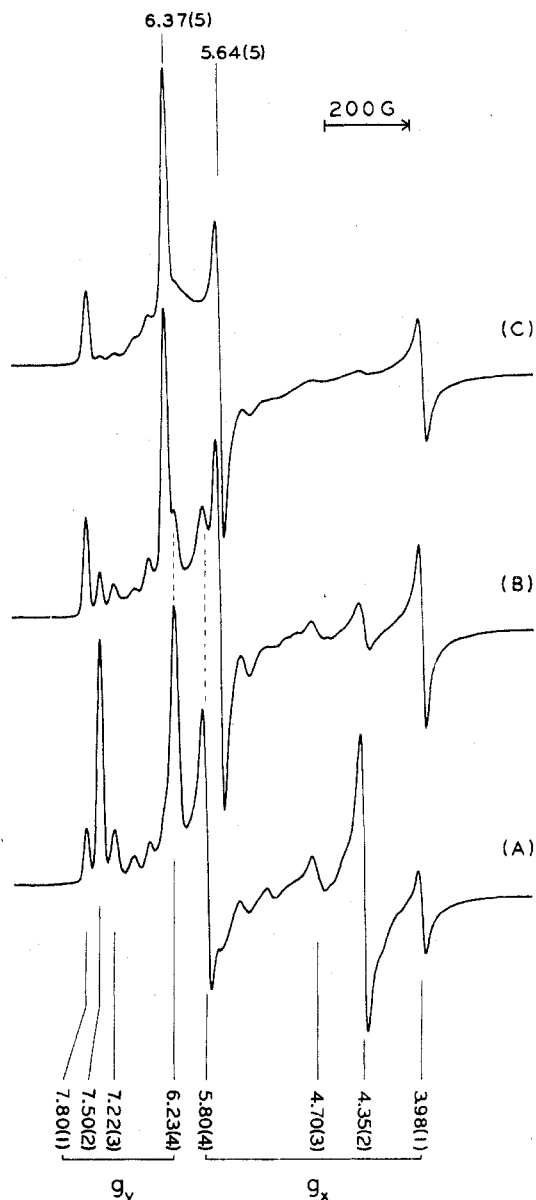
Figure 2. Effect of the water content in the solvent acetone from which the mixed crystals are obtained. EPR spectra were taken at 8°K: (A) no added H_2O; (B) 10% H_2O by volume; (C) 33% H_2O by volume.

Figure 3. EPR spectra of the mixed crystals observed at 5.5°K: (A) $TPPH_2(FeF)$ and (B) $TPPH_2(FeCH_3COO)$, both from acetone. Only the less distorted peaks are affected by the anion.

do contribute in forming the moderately distorted crystal field.

The effect of varying the water content in the solvent has a marked effect on the intensity distribution as shown in Figure 2, where the peaks belonging to the most rhombic species increased its intensity relative to others, and one of the least rhombic species (6.23, 5.80, 2.00) is replaced by a new set (6.37, 5.64, 2.00). Comparison made in the systems with different original anions (e.g., $TPPH_2(FeF)$, $TPPH_2$-($FeCH_3COO$)) shows that only the peaks belonging to the less distorted species exhibit the difference due to the anion. This means that the type of anion is not a significant factor in the formation of the more distorted rhombic environment.

It is most important to note in Figure 3 that of all the absorptions of $TPPH_2(FeF)$, only the one with smallest rhombicity (g = 6.24, 5.77, 2.00) shows the nuclear hyperfine splitting due to ^{19}F with A_y = 25.5 G, A_x = 27.0 G, and A_z = 45.3 G, while those with larger rhombicities do not give any indication of the splitting or line broadening of the same origin. The above hyperfine splitting is comparable in magnitude to that found in metmyoglobin fluoride.[14] Thus the original axial
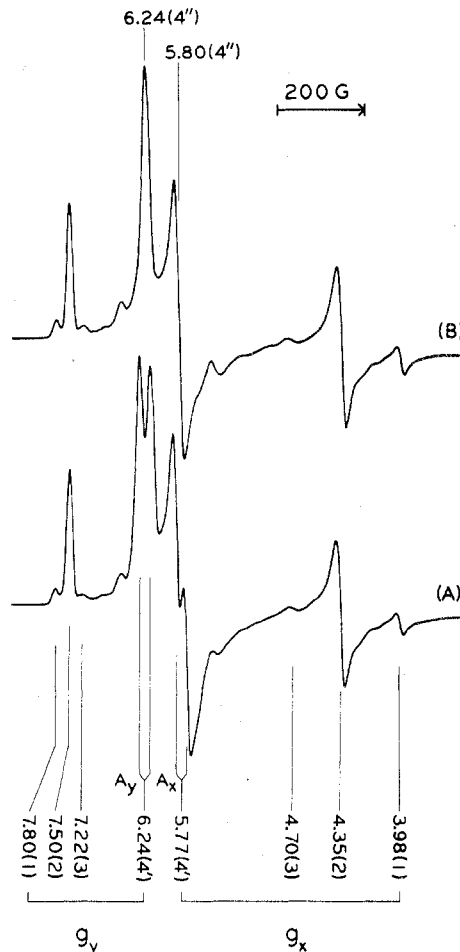
ligand, F⁻, on the fifth coordination site appears to be retained intact in the least distorted species but not in those with larger rhombicity. In fact addition of a small amount of Cl⁻ or F⁻ to the solvents causes disappearance of all but the least rhombic absorption which shows, in the case of F⁻, the hyperfine splitting. On this basis the preferential formation of the species with the highest rhombicity as the result of increasing the water content of the solvent acetone may be partly ascribed to the ease with which the axial ligand can be removed or displaced in a more proteolytic solvent. The notion of the dissociated fifth ligand is also consistent with the fact that the formation of the highly rhombic species is observed only when the crystals are formed from the polar solvents acetone, methanol, etc., and none of the precipitates similarly obtained from nonpolar solvents such as chloroform, hexane, benzene, xylene, or their mixtures exhibit the rhombicity higher than 3%. The complete dissociation of the axial ligand has been proven for hemin chloride in DMSO.[15]

The EPR spectra observed here are invariant when the corresponding compounds are left in the open air at room temperature for a period of several months; however, heat treatment in vacuo (200° for 36 hr) causes a loss of signal for all species except the one in which g = 6.33, 5.70, and 2.00. This latter species may be similar in the crystal field distortion to the one observed in the precipitate from acetone with high water content.

These findings, together with the fact that the rhombic EPR spectra are observed only in the presence of $TPPH_2$, seems to indicate that the rhombic character arises from the crystal packing forces of the free porphine, variously modified by the

solvent molecules as well as the anions included in the crystal. Mass spectrometry shows that the crystals obtained from acetone indeed contain some acetone even after exhaustive drying in vacuo. The effect of the crystal packing force has been cited to explain the observed rhombicity, though much smaller, of the hemin chloride in perylene single crystals.[13] A substantial deviation from D_4 molecular symmetry has been demonstrated for TPPH2 single crystals by X-ray studies.[16,17] Our further contention is that in at least the most distorted species the original anion is removed or displaced from the normal fifth coordination site of Fe[III]TPP. It is worth noting that the large rhombic distortion can be effected without invoking some specific axial ligand such as a sulfhydryl group, which is widely implicated in cytochrome P-450. Further studies are under way.

Registry No. TPPH2, 917-23-7; TPPFe[III]F, 55428-47-2; TPPFe[III]Cl, 16456-81-8; cytochrome P-450, 9035-51-2; TPPFe[III]CH3COO, 33393-26-9.

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Reaction of Phenylboron Dichloride with Cyclopentadienyldicarbollylcobalt

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Alkyl- or arylboron dihalides have been shown to react with cobaltocene to yield a borinatocobalt complex {[1-C6H5-(η^6-C5BH5)]Co(η^5-C5H5)}+.[1,2] The C2B9H11[2-] ions are icosahedra less one boron atom and can readily replace C5H5⁻ in metal complexes; they also react with alkyl- or arylboron dihalides to yield neutral B-substituted carboranes (eq 1).[3,4]
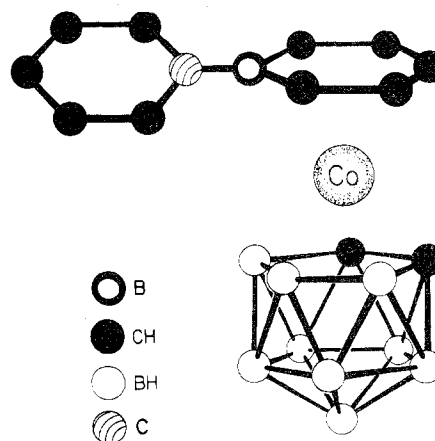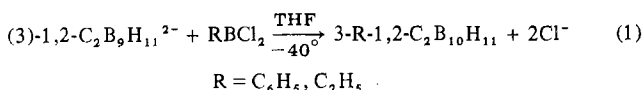
$$(3)\text{-}1,2\text{-}C_2B_9H_{11}{}^{2-} + RBCl_2 \xrightarrow[-40°]{THF} 3\text{-}R\text{-}1,2\text{-}C_2B_{10}H_{11} + 2Cl^- \quad (1)$$

$$R = C_6H_5, C_2H_5$$

Figure 1. Proposed structure of 3-[1-C6H5(η^6-C5BH5)]-3,1,2-Co(η^5-C2B9H11).

In our studies we reduced 3-(η^5-C5H5)-3,1,2-Co(η^5-C2B9H11), I, with sodium and then added C6H5BCl2, with the hope of inserting a C6H5B vertex into the carborane cage to produce a 13-vertex metallocarborane. Instead the phenylborinato complex 3-[1-C6H5(η^6-C5BH5)]-3,1,2-Co(η^5-C2B9H11), II, was formed exclusively (Figure 1).

Results and Discussion

Reduction of I was effected with 3 equiv of Na in the presence of naphthalene in tetrahydrofuran at room temperature. Excess C6H5BCl2 was then carefully added at low temperature. After work-up in air the only products isolated were the red borinato complex, II, and unreacted I. Compound II had a cutoff at m/e 346 in its mass spectrum corresponding to the $^{11}B_{10}{}^{12}C_{13}{}^{1}H_{21}{}^{59}Co^+$ ion. The 80.5-MHz ^{11}B NMR spectrum in CDCl3 exhibited a broad singlet at ~23.4 and doublets nearly coincidental with those in I of relative areas 1:1:4:2:1 at −8.1, −5.4, +4.8, +15.6, and +22.1 [ppm, relative to BF3·OEt2]. The 60-MHz ^{1}H NMR spectrum in CDl3 exhibited a singlet at τ 5.8 due to carborane C–H, two multiplets of the phenyl group at τ 2.0 and 2.6, and two multiplets of the borinato ring at τ 3.4 and 3.8. The complex splitting pattern in the aromatic region was nearly identical with that of {[1-C6H5(η^6-C5BH5)]Co(η^5-C5H5)}+.[1] Both the ^{1}H and ^{11}B NMR data clearly indicate that the phenyl-substituted boron atom has inserted in the cyclopentadienyl ring rather than the dicarbollide cage. There was no evidence for the formation of 13-vertex metallocarboranes. It is possible that 13-vertex polyhedra are so energetically unfavorable relative to the icosahedron that they cannot be formed from arylboron dihalides. This suggestion is supported by the fact that C2B10H12[2-] is also unreactive toward C6H5BCl2.

Experimental Part

Phenylboron dichloride was vacuum distilled and then further purified by several cycles of freezing, evacuation with high vacuum, and thawing immediately prior to use. Cyclopentadienyldicarbollylcobalt was prepared according to the literature.[5] Infrared spectra were determined using a Perkin-Elmer Model 137 spectrophotometer. Proton NMR spectra were obtained on a Varian T-60 spectrometer; 80.5-MHz ^{11}B NMR spectra were recorded on an instrument designed by Professor F. A. L. Anet.

3-[1-C6H5(η^6-C5BH5)]-3,1,2-Co(η^5-C2B9H11). Cyclopentadienyldicarbollylcobalt (1.0 g, 3.9 mmol) was dissolved in 100 ml of tetrahydrofuran in a nitrogen-flushed 3-neck, 250-ml flask. Sodium (0.27 g, 12 mg-atoms) and naphthalene (0.2 g, 1.5 mmol) were added and the reaction mixture was stirred for 24 hr. The flask was connected as the receiver to an alembic distillation apparatus and 2 ml of phenylboron dichloride was vacuum distilled directly into the receiver which was frozen with liquid nitrogen. The reaction vessel was warmed to −40° and stirred at that temperature for 2 hr and then