ruple splitting can be readily determined and reasonably precise values obtained should be of great importance, since NQR results frequently are not obtainable.

The Mössbauer data lead one to the conclusion that a great majority of Ph_4SbX compounds do not contain a simple tetrahedral Ph_4Sb^+ cation in the solid state. In some cases there is considerable covalent character to the Sb–X bond, in others the effect of the X group might be best described as causing distortion of the Ph_4Sb^+ group, and finally in a few cases the Ph_4Sb^+ cation does exist. Of the compounds studied only tetraphenylstibonium perchlorate belongs to this last category. The experimental observation that the isomer shift for the ionic Ph_4SbClO_4 corresponds to the largest s electron density in the Ph_4SbX series requires some comment. The tetrahedral bonding in the Ph_4Sb^+ cation would be described as sp^3. Pentacoordinate bonding, such as required in a covalent Ph_4SbX molecule, would be described as some sort of dsp^3 hybridization. Significantly, the basic s electron density and p shielding should be identical for these two types of hybridization. In the case of pentacoordinate bonding, as in covalent Ph_4SbX, the Sb–X bond should have some s character. If X is an electronegative group, it should withdraw electrons along the bond, thus reducing the s density at Sb. This electron withdrawal would not occur for a $Ph_4Sb^+ X^-$ ionic compound, and thus the Ph_4Sb^+ cation would have the largest s electron density at Sb and the lowest value for the isomer shift in a series Ph_4SbX.

The general observation that the isomer shifts for the Ph_3SbX_2 series are lower than for the corresponding members of the Ph_4SbX series indicates either more s density at the antimony in the Ph_3SbX_2 series or less p density. It is difficult to imagine how the substitution of an electronegative X group for a phenyl could increase electron density at antimony. The situation is complicated by the possibility of variations in geometry and hybridization in the Ph_4SbX series. However, both isomer shift and quadrupole splitting data are in agreement that the Ph_3SbX_2 compounds have less p electron density. The p density would be removed along the apical Sb–X bonds, giving rise to the characteristically large negative quadrupole splitting observed in these compounds.

It is apparent from the results presented above that ^{121}Sb Mössbauer studies of organoantimony compounds, especially at liquid helium temperature, can be valuable in structural analysis of these compounds. Indeed, the variations observed appear considerably more sensitive than those reported for ^{119}Sn in organotin compounds.

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An Electron Spin Resonance Study of Coordination to the Fifth and Sixth Positions of α,β,γ,δ-Tetra(*p*-methoxyphenyl)porphinatocobalt(II)

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Abstract: Esr studies of α,β,γ,δ-tetra(*p*-methoxyphenyl)porphinatocobalt(II) in toluene glasses in the presence of various concentrations of a number of different amines show the formation of both five- and six-coordinate complexes. The esr parameters are quite insensitive to the basicity of the amine, and the resolution of the spectrum is determined by the composition of the glass. In the presence of air, the esr spectrum undergoes a dramatic change, attributed to the formation of a six-coordinate complex containing one amine and one oxygen molecule as the fifth and sixth ligands.

Several esr studies of planar, square-pyramidal, and octahedral low-spin cobalt(II) complexes have indicated the sensitivity of their esr parameters to solvation or crystalline environment.[2-6] This has been attributed to the fact that the single unpaired electron is in the d_{z^2} orbital of cobalt.[2,3,5] Assour[3] has correlated bonding parameters of cobalt phthalocyanine [Co(pc)] obtained from glassy spectra with the electronegativity of the amine solvent. In the present study of α,β,γ,δ-tetra(*p*-methoxyphenyl)porphinatocobalt(II) [Co(*p*-OCH_3)TPP] it was found that the esr spectrum was extremely sensitive to the quality of the glass, and because of this a common solvent (toluene), which is known to form good glasses, was used for all samples, with various amounts of amines added as ligands. The purpose of this study was to determine the esr parameters ($g_{||}$, $g_{\perp}$, $A_{||}$, $A_{\perp}$, A_N) of a number of different cobalt–porphyrin complexes in a common medium in order to isolate the specific effects due to coordination from

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possible bulk solvent effects such as poor glass formation or bulk electronegativity effects. With such data available it will be possible to evaluate existing theories[5,7] which attempt to explain the variation in observed esr parameters for low-spin d^7 complexes.[8]

Experimental Section

Tetra(*p*-methoxyphenyl)porphyrin [H_2(*p*-OCH_3)TPP] was prepared by the method of Adler, *et al.*[9] Pyrrole (7.1 ml, 0.1 mol) and 12.1 ml of anisaldehyde (0.1 mol) were refluxed in 750 ml of propionic acid for 30 min. The porphyrin usually crystallized upon cooling, but occasionally it was necessary to add about 150 ml of ether to bring about rapid crystallization. The product was filtered, washed with methanol, and chromatographed on silica gel (Baker, chromatographic grade) with reagent grade chloroform. The yield of purified product was 17%. The cobalt adduct was prepared by refluxing 0.7 g of crude H_2(*p*-OCH_3)TPP and 2.5 g of Co(acetate)$_2$ in 50 ml of propionic acid for 30 min, filtering, and washing with methanol. The product was purified by column chromatography as above. Only the center of the reddish purple band was collected each time, and no attempt was made to exclude oxygen from the purification procedure. After five successive chromatographings the extinction coefficients of the uv-visible spectral bands had reached constant values at 5300 (1.660×10^4), 4140 (2.58×10^5), ~3300 (shoulder, 1.03×10^4), and 2640 Å (2.70×10^4). Vacuum sublimation of this sample using a tube with a temperature gradient from 350 to 300° caused deterioration, possibly owing to hot spots in the sublimation tube. The visible spectrum of the sublimed sample indicated the possible presence of chlorin. Upon rechromatographing this sample, four bands were observed on the column, the first and largest of which had the same spectral bands and extinction coefficients as observed before sublimation. If the chromatographed sample was crystallized from chloroform by slow evaporation of solvent at room temperature the chloroform monosolvate (I) was obtained.

Anal. Calcd for $CoC_{48}H_{23}H_{36}N_4O_4 \cdot CHCl_3$: Co, 6.47; C, 64.60; H, 4.06; N, 6.15; Cl, 11.69. Found: Co, 6.60; C, 64.30. H, 3.95; N, 6.03; Cl, 11.49.

If the above crystals were heated to 100° for 30 min (II), or if the compound was recrystallized from benzene (III) the crystals contained essentially no solvent molecules.

Anal. Calcd for $CoC_{48}H_{36}N_4O_4$: Co, 7.25; C, 72.86; H, 4.55; N, 7.08; Cl, 0. Found (for II): Co, 7.19; C, 72.78; H, 4.46; N, 6.96; Cl, 0.13. Found (for III): Co, 7.21; C, 72.93; H, 4.63; N, 6.80; Cl, 0.25.

A mass spectrum of a pure sample of II showed less than 0.1% impurity of higher molecular weight (805 g/mol) than Co(*p*-OCH_3)TPP (791 g/mol), and the fractions of heavier isotopes were close to the expected values. The mass spectrum showed no evidence of the presence of free porphyrin.

The purified Co(*p*-OCH_3)TPP was stored under vacuum in the dark, and further chromatographings during the course of this study showed that little additional sample deterioration took place as a function of time. Other cobalt porphyrins used in this study were prepared by reaction of the appropriately substituted benzaldehyde with pyrrole according to the above procedure, and were purified in the same way as was Co(*p*-OCH_3)TPP. All samples used for polycrystalline spectra were crystallized from benzene prior to use.

Toluene was purified by distillation from sodium metal, and all amines except quinuclidine were distilled from zinc dust and then from anhydrous barium oxide. Quinuclidine was obtained from Aldrich Chemical Co. as the hydrochloride. It was dissolved in aqueous sodium hydroxide, extracted into benzene, dried over Na_2SO_4, and collected by evaporation of benzene. Solutions of amines in toluene were prepared by standard volumetric techniques.

Esr samples were prepared on a vacuum line by degassing the solvent or 0.25 ml of solution by the usual freeze-pump-thaw method and then vacuum distilling 0.25 ml into the quartz sample tube containing about 1 mg of Co(*p*-OCH_3)TPP, which gave sample concentrations in the range of 0.005 *M*. The tubes were then sealed and the esr spectra were recorded at 77°K on either a Varian V-4502 or E-3 esr spectrometer, each with 100-kHz field modulation of no more than 0.1 of the observed line widths for each spectrum (in gauss). The frequency was measured using DPPH ($g = 2.0036$). Field sweep calibration using an nmr probe was used on the V-4502 spectrometer, and the parameters calculated from the E-3 spectra agreed with the former to within the experimental error reported.

Calculations

The esr spectrum of an axially symmetric molecule with one interacting nucleus with spin (I, m_I) is given by the relation[10]

$$h\nu = g\beta H + Km_I + \frac{A_\perp^2}{4g\beta H_0}\left(\frac{A_\parallel^2 + K^2}{K^2}\right)[I(I+1) - m_I^2] + \frac{1}{2g\beta H_0}\left(\frac{A_\parallel^2 - A_\perp^2}{K}\right)^2\left(\frac{g_\parallel g_\perp}{g^2}\right)^2 \sin^2\theta \cos^2\theta m_I \quad (1)$$

where

$$K^2g^2 = A_\parallel^2 g_\parallel^2 \cos^2\theta + A_\perp^2 g_\perp^2 \sin^2\theta \quad (2)$$

$$g^2 = g_\parallel^2 \cos^2\theta + g_\perp^2 \sin^2\theta \quad (3)$$

θ is the angle between the unique (parallel) molecular axis and the applied field, H. Third-order and quadrupole effects have been neglected in this treatment. $g_\parallel$ and $g_\perp$ are components of the g tensor, and $A_\parallel$ and $A_\perp$ are components of the hyperfine interaction. Only the absolute values of the splitting constants can be obtained from the glassy spectrum; it will be assumed that m_I is positive at the high-field end of the spectrum. For the parallel ($\theta = 0°$) and perpendicular ($\theta = 90°$) orientations

$$\frac{h\nu}{g_\parallel\beta} = H_\parallel + a_\parallel m_I + \frac{a_\perp^2 g_\perp^2}{2g_\parallel^2 H_\parallel}[I(I+1) - m_I^2] \quad (4)$$

and

$$\frac{h\nu}{g_\perp\beta} = H_\perp + a_\perp m_I + \frac{(a_\perp^2 g_\perp + a_\parallel^2 g_\parallel^2)}{4g_\perp^2 H_\perp}[I(I+1) - m_I^2] \quad (5)$$

where

$$a = A_i/g_i\beta \quad (6)$$

Solving these expressions for the observed spacings ($\Delta H_\parallel$ and $\Delta H_\perp$) between hyperfine lines we obtain

$$\Delta H_\parallel = a_\parallel + \frac{a_\perp^2 g_\perp^2(2m_I - 1)}{2H_{0\parallel}g_\parallel^2} \quad (7)$$

$$\Delta H_\perp = a_\perp + \frac{(a_\parallel^2 g_\parallel^2 + a_\perp^2 g_\perp^2)(2m_I - 1)}{4H_{0\perp}g_\perp^2} \quad (8)$$

where the units of $a_\parallel$ and $a_\perp$ are gauss, and m_I refers to the higher field component. One can calculate $a_\parallel$ and $a_\perp$ directly from eq 7 and 8.

The calculation of parameters from the types of esr spectra discussed below and shown in Figures 1–6 depended upon the resolution of the particular spectrum. Except for the five-coordinate complexes (Figure 3a), where $A_\perp$ is too small to be resolved, values of $A_\perp$ and $g_\perp$ could be obtained from the spectra using eq 8 and 5. For the five-coordinate complexes an upper limit on the value of $A_\perp$ was estimated from the

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Table I. Esr Parameters for a Number of Low-Spin Four-, Five-, and Six-Coordinate Cobalt–Porphyrin Complexes

System	$g_\perp$[a]	$g_\parallel$[a]	$\lvert A_\perp \rvert$,[b] cm^{-1}	$\lvert A_\parallel \rvert$,[b] cm^{-1}	$\lvert A_N \rvert$,[b] cm^{-1}	Ref
Co(*p*-OCH_3)TPP[c]						
concd polycrystal	3.285[d]	1.79[e]	0.0394[f]	0.0147[g]		*h*
in Ni(*p*-OCH_3)TPP	3.317[d]	1.75[e]	0.0403[f]	0.0195[g]		*h*
in H_2(*p*-OCH_3)TPP	3.264[d]	1.81[e]	0.0374[f]	0.0171[g]		*h*
Co(*p*-CH_3)TPP[c]						
in H_2(*p*-CH_3)TPP	3.193[d]	1.84[e]	0.0352[f]	0.0173[g]		*h*
Co(*m*-CH_3)TPP[c]						
concd polycrystal	3.344[d]	1.75[e]	0.0402[f]	0.0618[g]		*h*
Co(*o*-CH_3)TPP[c]						
concd polycrystal	2.875[d]	1.97[e]	0.0235[f]	0.0139[g]		*h*
Co(pc)[c]						
in α-Zn(pc)	2.422	2.007	0.0066	0.0116		*i*
in β-Ni(pc)	2.94	1.89	0.028	0.015		*i*
CoTPP[c]						
in H_2TPP	3.322	1.798	0.0315	0.0197		*j*
Co(*p*-OCH_3)TPP[c] in toluene	2.848	2.006	0.0228	0.0161		*h*
+ 1 pyridine	≥2.327	2.025	≤0.0012[k]	0.00798	0.00156[l]	*h*
+ 1 2-picolone	≥2.324	2.027	≤0.0011[k]	0.00780	0.00155[l]	*h*
+ 1 3-picoline	≥2.326	2.028	≤0.0011[k]	0.00787	0.00156[l]	*h*
+ 1 4-picoline	≥2.323	2.028	≤0.0011[k]	0.00789	0.00161[l]	*h*
+ 1 3,4-lutidine	≥2.318	2.027	≤0.0011[k]	0.00774	0.00163[l]	*h*
+ 1 3,5-lutidine	≥2.316	2.029	≤0.0011[k]	0.00764	0.00161[l]	*h*
+ 1 collidine[c]	≥2.324	2.027	≤0.0011[k]	0.00787	0.00152[l]	*h*
+ 1 quinoline	≥2.325	2.032	≤0.0010[k]	0.00783	0.00159[l]	*h*
+ N-CH_3 imidazole	≥2.314	2.033	≤0.0012[k]	0.00759	0.00163[l]	*h*
+ 1 pyrrole	≥2.323	2.028	≤0.0011[k]	0.00774	0.00161[l]	*h*
+ 1 piperidine	≥2.318	2.026	≤0.0013[k]	0.00774	0.00151[l]	*h*
+ 1 quinuclidine[c]	≥2.322	2.032	≤0.0011[k]	0.00812	0.00131[l]	*h*
+ 1-*n*-hexylamine	≥2.311	2.022	≤0.0010[k]	0.00782	0.00149[l]	*h*
Vitamin B_{12r}						
+ 1 imidazole	2.27	2.022	*k*	0.00944	0.00170	*m*
Co(Dmg)$_2$[c] + 1 imidazole	2.272	2.025	*k*	0.00822	0.00170	*m*
Co(pc)[c] in pyridine	2.268	2.016	*k*	0.0078	0.00114	*n*
Co(Dmg)$_2$[c] + 2 pyridine	2.29	2.023	*k*	0.0080	0.00115	*m*
Co(*p*-OCH_3)TPP[c] in toluene						
+ 2 pyridine	2.216	2.047	0.00570	0.0060[f]	0.00112	*h*
+ 2 2-picoline	*o*	*o*	*o*	*o*	*o*	*h*
+ 2 3-picoline	2.228	2.058[e]	0.00544	0.0061[f]	*p*	*h*
+ 2 4-picoline	2.226	2.060[e]	0.00500	0.0061[f]	*p*	*h*
+ 2 3,4-lutidine	2.226	2.057[e]	0.00605	0.0060[f]	*p*	*h*
+ 2 3,5-lutidine	2.228	2.062[e]	0.00521	0.0066[f]	0.00146	*h*
+ 2 collidine[c]	*o*	*o*	*o*	*o*	*o*	*h*
+ 2 quinoline	*o*	*o*	*o*	*o*	*o*	*h*
+ 2 N-CH_3 imidazole	*o*	*o*	*o*	*o*	*o*	*h*
+ 2 pyrrole	*o*	*o*	*o*	*o*	*o*	*h*
+ 2 piperidine	2.214	2.054[e]	0.00538	0.0061[f]	*p*	*h*
+ 2 quinuclidine[c]	~2.299	2.027	≤0.0023[k]	0.00805	0.00095[l]	*h*
+ 2 *n*-hexylamine	2.208	2.067[e]	≤0.00618	0.0072[f]	*p*	*h*
Co(*p*-OCH_3)TPP[c] in toluene glasses in the presence of O_2						
+ 1 pyridine	2.002	2.077	0.00107[q]	0.00166[q]	*p*	*h*
+ 1 2-picoline	2.000	2.076	0.00107[q]	0.00163[q]	*p*	*h*
+ 1 3-picoline	2.000	2.073	0.00099[q]	0.00161[q]	*p*	*h*
+ 1 4-picoline	2.001	2.074	0.00103[q]	0.00164[q]	*p*	*h*
+ 1 3,4-lutidine	2.001	2.074	0.00096[q]	0.00159[q]	*p*	*h*
+ 1,3,5-lutidine	2.001	2.073	0.00098[q]	0.00158[q]	*p*	*h*
+ 1 collidine[c]	1.998	2.076	0.00099[q]	0.00163[q]	*p*	*h*
+ 1 quinoline	2.002	2.074	0.00103[q]	0.00163[q]	*p*	*h*
+ 1 N-CH_3 imidazole	2.002	2.080	0.00098[q]	0.00162[q]	*p*	*h*
+ 1 pyrrole	2.004	2.081[k]	0.00107[q]	0.00184[q]	*p*	*h*
+ 1 piperidine	2.002	2.076	0.00104[q]	0.00164[q]	*p*	*h*
+ 1 quinuclidine[c]	1.998	2.074	0.00121[q]	0.00162[q]	*p*	*h*
+ 1 *n*-hexylamine	2.002	2.077	0.00100[q]	0.00159[q]	*p*	*h*
Vitamin B_{12r} + O_2	2.004	2.07	0.00122	0.00145	*p*	*r*

[a] *g* values to ±0.001 unless otherwise noted. [b] *A* values to ±0.0001 cm^{-1} unless otherwise noted. [c] (*p*-OCH_3)TPP = tetra(*p*-methoxyphenyl)porphyrin; (*p*-CH_3)TPP = tetra(*p*-methylphenyl)porphyrin; (*m*-CH_3)TPP = tetra(*m*-methylphenyl)porphyrin; (*o*-CH_3)TPP = tetra(*o*-methylphenyl)porphyrin; pc = phthalocyanine; TPP = tetraphenylporphyrin; dmg = dimethylglyoxime; quinuclidine = 1,4-ethylenepiperidine; collidine = 2,4,6-trimethylpyridine. [d] ±0.003. [e] ±0.01. [f] 0.003 cm^{-1}. [g] ±0.001 cm^{-1}. [h] This work. [i] Reference 5. [j] Reference 2. [k] Co hfs unresolved. Estimates based on total line width. [l] ±0.00005 cm^{-1}. [m] Reference 4. [n] Reference 3. [o] Complex did not form. [p] N shfs unresolved. [q] ± 0.00002 cm^{-1}. [r] Reference 6.

peak to peak width of the envelope, and a lower limit on the value of $g_\perp$ was estimated from the point at which the derivative crossed the base line. Because the parallel branch of the spectrum was partially obscured by the perpendicular lines in the polycrystalline samples (Figure 1) and six-coordinate complexes (Figure 3b), and because of the broadness of the parallel lines in all but the five-coordinate complexes and oxygen

Table II. Substituent Effects on the Esr Parameters of the Five-Coordinate Pyridine Adduct and the Six-Coordinate Pyridine–O_2 Adduct of Cobalt Tetraphenylporphyrin

Compound[a,b]	$g_\perp$[c]	$g_\parallel$[c]	$\lvert A_\perp \rvert$,[d] cm^{-1}	$\lvert A_\parallel \rvert$,[d] cm^{-1}	$\lvert A_N \rvert$,[e] cm^{-1}
CoTPP·pyridine	2.324	2.027	0.0013[f]	0.00789	0.00142
Co(p-OCH_3)TPP·pyridine	2.327	2.025	0.0012[f]	0.00798	0.00156
Co(p-CH_3)PP·pyridine	2.326	2.025	0.0012[f]	0.00795	0.00156
Co(m-CH_3)TPP·pyridine	2.326	2.025	0.0013[f]	0.00795	0.00156
Co(o-CH_3)TPP·pyridine	2.326	2.025	0.0016[f]	0.00820	0.00156
Co(p-Cl)TPP·pyridine	2.324	2.025	0.0012[f]	0.00789	0.00151
Co(p-CN)TPP·pyridine	2.323	2.027	0.0011[f]	0.00785	0.00156
CoTPP·pyridine·O_2	2.003	2.072	0.00107[g]	0.00158[g]	
Co(p-OCH_3)TPP·pyridine·O_2	2.002	2.077	0.00107[g]	0.00166[g]	
Co(p-CH_3)TPP·pyridine·O_2	2.002	2.074	0.00108[g]	0.00165[g]	
Co(m-CH_3)TPP·pyridine·O_2	2.002	2.074	0.00108[g]	0.00167[g]	
Co(o-CH_3)TPP·pyridine·O_2	2.003	2.074	0.00109[g]	0.00167[g]	
Co(p-Cl)TPP·pyridine·O_2	2.002	2.073	0.00106[g]	0.00164[g]	
Co(p-CN)TPP·pyridine·O_2	2.002	2.073	0.00103[g]	0.00155[g]	

[a] The substituents on the phenyl rings of cobalt tetraphenyl porphyrin are designated by the terms in parentheses. [b] All samples in 0.0621 M pyridine. [c] ± 0.001. [d] ± 0.0001 cm^{-1} unless otherwise noted. [e] ± 0.00005 cm^{-1}. [f] Co hfs unresolved. Estimates based on total line width. [g] ± 0.00002 cm^{-1}.

adducts (Figure 6), the parameters calculated for the parallel spectra in these cases are somewhat less accurate (see footnotes, Table I) than the others.

Extra absorption peaks[11] were observed in the spectra of the five-coordinate quinuclidine adduct (see Figure 4), the five-coordinate piperidine and n-hexylamine adducts, and most of the oxygen adducts (see Figure 6).

Results

The parameters calculated from the esr spectra of the systems studied are listed in Table I and II, along with a sampling of the data for similar systems reported by other investigators. Each type of spectrum observed is described below.

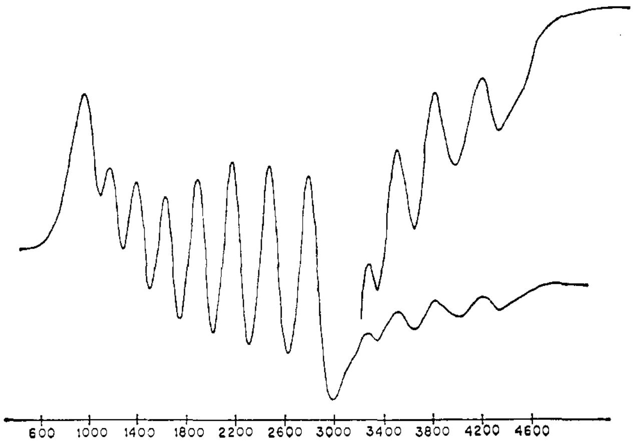

Figure 1. Esr spectrum of polycrystalline Co(p-OCH_3)TPP; ν = 9118 MHz, field in gauss.

Polycrystalline Co(p-OCH_3)TPP. The spectrum of the undiluted sample is shown in Figure 1. It is similar to that obtained by Assour[2] for CoTPP diluted in H_2TPP except that it shows no extraneous spectrum near g = 2 and the parameters listed in Table I are somewhat different. The chloroform monosolvate (I) gave a very similar esr spectrum ($g_\perp$ = 3.302, $g_\parallel$ = 1.72, $A_\perp$ = 0.0406 cm^{-1}, $A_\parallel$ = 0.0173 cm^{-1}), but the sample which was heated to remove chloroform (II) showed a more complex pattern of lines, probably owing to partial transformation from one crystalline form to another. The spectrum of a sample of the undiluted polycrystalline material showed no change over a 9-month period. A resonance at g = 2 was observed for Co(p-OCH_3)TPP diluted in H_2(p-OCH_3)-TPP or Ni(p-OCH_3)TPP, but its intensity was a function of the purity of the host porphyrin rather than the presence of oxygen as suggested by Assour and Kahn[5] for cobalt phthalocyanine in various host crystals. The presence of oxygen in the sample tubes did not seem to affect the spectrum over a short time period, but on reexamination after 9 months the sample of Co complex diluted in H_2(p-OCH_3)TPP showed at least four overlapping spectra: the original one; a sharper set of lines with $g_\perp \sim 3.51$, $g_\parallel \sim 1.71$, and similar splitting constants; and evidence of at least two other species in smaller concentrations. The sample of Co complex diluted in Ni(p-OCH_3)TPP showed two sets of lines roughly equivalent to the two strongest sets observed in the spectrum of the sample diluted in H_2(p-OCH_3)TPP. These new sets of lines are either due to decomposition in the presence of oxygen, or to partial transformation from one crystalline form to another. None of the sets of lines men-

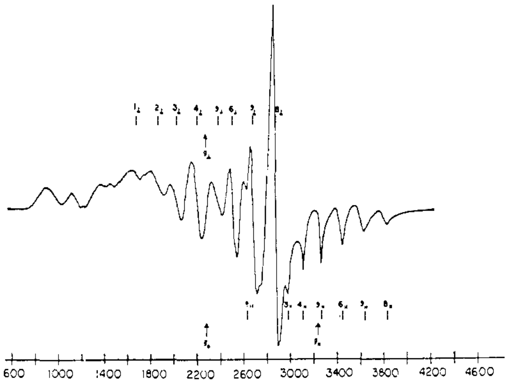

Figure 2. Esr spectrum of 0.001 M Co(p-OCH_3)TPP in toluene glass; ν = 9132 MHz, field in gauss. The peaks between 800 and 1600 G are attributed to the presence of some polycrystalline material.

[11] R. Neiman and D. Kivelson, *J. Chem. Phys.*, 35, 156 (1961).

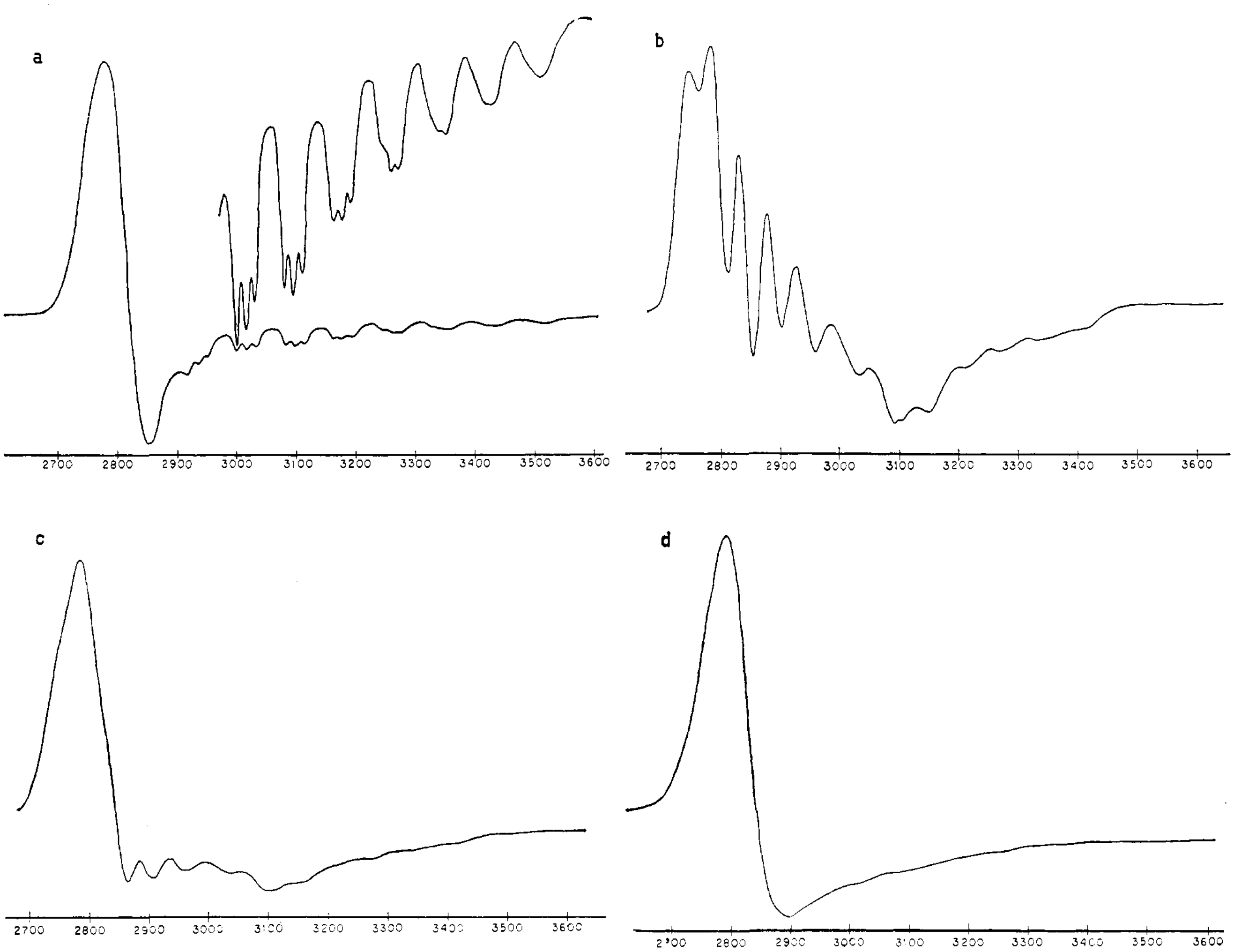

Figure 3. Esr spectra of 0.005 *M* Co(p-OCH$_3$)TPP in toluene–pyridine glasses; ν = 9132 MHz, field in gauss. Concentrations of pyridine in toluene are (a) 0.0621 *M*, (b) 6.21 *M* (50% volume composition), (c) 12.29 *M*(99%), (d) 12.41 *M*(100%).

tioned above seems consistent with the formation of an oxygen complex, because their splitting constants are much larger than those reported for oxygen adducts. (See section on oxygen complexes and ref 6 and 12.)

Co(p-OCH$_3$)TPP in Toluene Glass. The complex pattern of lines observed for this sample is shown in Figure 2. This spectrum was by far the most difficult to obtain and analyze, mainly because of the low solubility (2×10^{-4} *M*) of the compound in pure toluene and the difficulty in obtaining good glasses. If the sample was cooled quickly in liquid nitrogen the spectrum was observed, but if it was then allowed to warm slightly above 77°K the spectrum disappeared and did not reappear upon recooling unless it was warmed to room temperature before recooling. The presence of trace amounts of water, oxygen, and other impurities produced marked changes in the observed splitting constants. However, the spectrum shown in Figure 2 was reproduced using samples of toluene from three different sources and did not change over a period of 9 months. The spectrum was also not affected by addition of a molar excess of free H$_2$(p-OCH$_3$)TPP, which suggests that this porphyrin does not form dimers,[13] at least in toluene solution.

Co(p-OCH$_3$)TPP + Amines in Toluene Glasses. The spectra of Co(p-OCH$_3$)TPP in the presence of various concentrations of pyridine in toluene glasses are shown in Figure 3. In dilute pyridine solution (up to a [Co]:[pyridine] ratio of approximately 1:20) the spectrum shown in Figure 3a is observed. The perpendicular splitting constant, determined from the width of the low-field envelope, must be less than or equal to 11 G, or 0.0012 cm^{-1}. The parallel components show superhyperfine (shf) splittings due to interaction with one nitrogen, which indicates that the species present in this concentration range is a 1:1 complex of Co(p-OCH$_3$)TPP with pyridine. Similar spectra are observed when a number of other amines are present.[14] These spectra are quite similar to those observed by Schrauzer and Lee[4] for vitamin B$_{12r}$ in aqueous solutions in the presence of various amines, where again the cobalt is expected to be bonded to one amine.[15] This does not rule out the possibility of weak solvation of the sixth position by a toluene molecule, but if such solvation does exist one would expect

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[12] B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Amer. Chem. Soc.*, **92**, 61 (1970).

[13] A. McCragh, C. B. Storm, and W. S. Koski, *ibid.*, **87**, 1470 (1965).

[14] Except in the case of the 1:1 complex with quinuclidine, which showed an extra absorption peak similar to those observed in many copper complexes[11] (see Figure 4a).

[15] A recent report [S. A. Cockle, H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Biochim. Biophys. Acta*, 177, 686 (1969)] points out that it is not possible, from the esr spectrum, to distinguish between five- and six-coordination in which the sixth ligand is a solvent molecule (water in their case).

much weaker Co–solvent interaction in toluene than in aqueous solution.[16]

As additional pyridine is added the spectrum changes from that shown in Figure 3a to that shown in Figure 3b. This spectrum exists over a large pyridine concentration range, with only minor changes in peak widths.

At very high concentrations of pyridine (90–99% solvent composition by volume, Figure 3c) the resolution is poorer, until in pure pyridine (Figure 3d) the spectrum has lost all detail. This effect is undoubtedly due to segregation or ordering of the Co(p-OCH$_3$)TPP molecules in solvent mixtures containing large proportions of pyridine. For some other amines, including 3,4- and 3,5-lutidine, n-hexylamine, and collidine (2,4,6-trimethylpyridine), the loss of spectral features begins at a lower amine concentration, *i.e.*, at 50% amine–toluene compositions. Collidine was a particularly interesting case, for it was found to form only a 1:1 adduct in up to 90% collidine (in distinction to the results of Assour[3] for Co(pc) in 2,6-lutidine). However, the perpendicular envelope became much sharper, and the intensity of the perpendicular envelope relative to the parallel lines increased so dramatically on going from 10 to 50% collidine, and then remained nearly constant above that point, that it was necessary to increase the signal level by a factor of 50 instead of the usual fivefold increase in order to observe the parallel lines clearly (see Figure 3a, where the magnification of the parallel lines is ten times rather than five). The parallel lines were, however, each clearly split into three components of equal intensity no matter what solvent composition was used, and they remained at exactly the same field positions. This indicates that the species present is the 1:1 complex throughout the range of solvent compositions studied, but that the quality of the glass is altered when substantial amounts of collidine are present.

A number of other solvents, some of which have been used in the past to observe glassy spectra, were tested with 10% pyridine–90% solvent compositions in the presence of Co(p-OCH$_3$)TPP and air as a comparison to the pyridine–toluene series shown in Figures 3a–d. The appearance of these spectra was similar to that shown in Figure 5, where the sharp spectrum in the center is due to an oxygen adduct which is discussed in the following section. The results are given in Table III. In general, the resolution of the spectrum of the oxygen adduct was much better than that of the 1:1 or 2:1 pyridine adducts. It would appear from the results shown in Table III and Figures 3a–d that solvent compositions of 10% pyridine–90% acetone, tetrahydrofuran, mineral oil, benzene, dimethyl sulfoxide, p-xylene, or pyridine are unacceptable for obtaining good glassy spectra of compounds such as those reported here. Unfortunately, Co(p-OCH$_3$)TPP was not soluble in 10% pyridine–90% ethanol, ethylene glycol, or aliphatic hydrocarbons, so these solvents could not be compared to the ones listed in Table III. In the pyridine–chloroform glass the spectrum of the five-coordinate complex was observed, probably because of solvation of a large fraction of the pyridine present by chloroform, which is known to have hydrogen-bonding capabilities. This spectrum was also observed in pyridine–diphenyl ether and pyridine–α-bromonaphthalene, possibly due to stronger solvation of the porphyrin by these aromatic ring systems.

Table III. Resolution of Spectra of Co(p-OCH$_3$)TPP in 10% Pyridine–90% Solvent Glasses at 77°K in the Presence of Oxygen, Placed in Approximate Order of Acceptibility as Solvents for Glass Spectra of Co(p-OCH$_3$)TPP(pyridine)$_2$

Solvent	Type of pyridine adduct spectrum observed	Resolution of O$_2$ complex spectrum
Toluene	3b	Very good
o-Xylene	3b	Good
α-Bromonaphthalene	3a	Good
Methylene chloride	3b	Good
Chlorobenzene	3b	Fair
Dioxane	3b	Good
m-Xylene	3c	Good
Diphenyl ether	3a	Fair
Chloroform	3a	Fair
Acetone	3d	Good
Tetrahydrofuran	3d	Fair
Mineral oil	3d	Fair
Benzene	3d	Fair
Dimethyl sulfoxide	3d	Poor
p-Xylene	3d	Poor
Pyridine	3d	Very poor

The species represented by the spectrum shown in Figure 3b exists in equilibrium with the five-coordinate 1:1 cobalt–amine complex. In intermediate amine concentration ranges overlapping esr spectra from the two species were observed, and equilibrium constants for successive complex formation at room temperature can be measured from visible spectral shifts.[17]

When piperidine, which is generally expected to be a stronger ligand, was substituted for pyridine, a much lower (a factor of 100) concentration of amine was necessary to shift from one spectrum to the other. Superhyperfine splittings are not generally observed in this type of spectrum, although the parallel (upfield) lines are broad enough to obscure a nitrogen splitting of similar magnitude to that observed for the 1:1 complex, and the lines most likely to show shf splittings were obscured by the perpendicular branch of the spectrum.

Despite the general absence of superhyperfine structure it would seem reasonable to attribute this spectrum to a 2:1 amine–Co(p-OCH$_3$)TPP complex. This spectrum is markedly different from those reported for Co(pc) in various amines.[3] In particular, for Co(p-OCH$_3$)TPP the perpendicular cobalt hyperfine structure is clearly resolved, and the parallel and perpendicular splitting constants are similar in magnitude. It should be noted, however, that because of the broadness of the parallel lines and the fact that half of them are obscured by the perpendicular lines, the accuracy in the determination of $A_{\parallel}$ and $g_{\parallel}$ is less than that of $A_{\perp}$ and $g_{\perp}$ (see Table I). The only sample which showed the type of spectrum reported by Assour[3] was that con-

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(16) The anisotropy in the g tensors and splitting constants of Co(p-OCH$_3$)TPP decreases on going from the polycrystalline state to a toluene glass, to toluene glasses containing amines (Table I), which is the expected order of increasing interaction along the z axis of cobalt. There is more similarity between the esr parameters of the toluene glass and the polycrystalline samples of Co(p-OCH$_3$)TPP than there is between the esr parameters of the toluene glass of Co(p-OCH$_3$)TPP and those of its amine adducts, a further suggestion of only very weak, if any, solvation of the axial positions of cobalt by toluene molecules.

(17) F. A. Walker, manuscript in preparation.

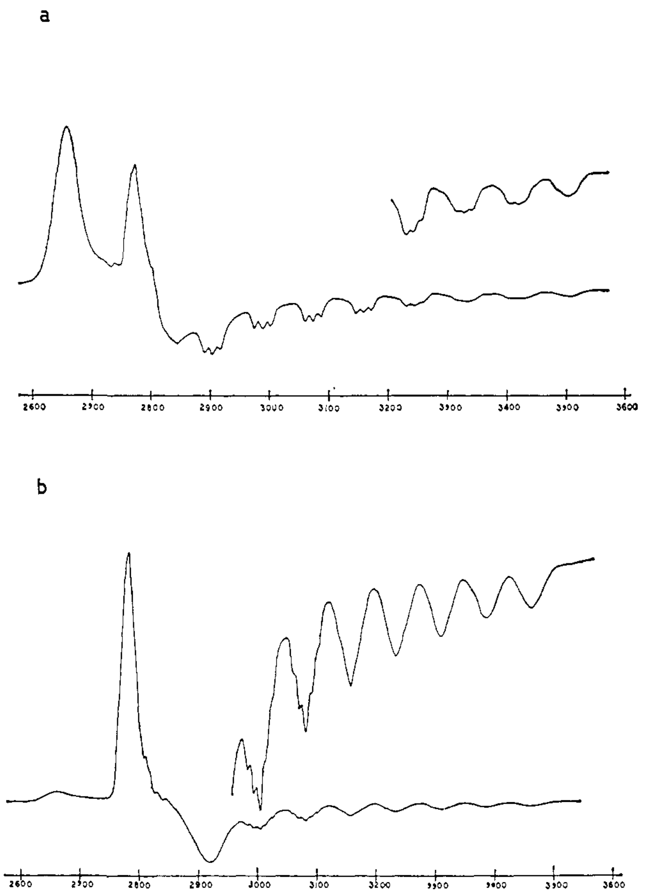

Figure 4. Esr spectra of 0.005 *M* Co(p-OCH$_3$)TPP in toluene containing (a) approximately 0.001 *M* quinuclidine and (b) approximately 1 *M* quinuclidine; ν = 9132 MHz, field in gauss. Spectrum a shows splittings due to interaction of the unpaired electron with one nitrogen and an extra absorption peak[9] not observed in other spectra of this type. Spectrum b shows splittings due to interaction of the unpaired electron with two nitrogens and a complex perpendicular envelope. The parallel line positions of the two spectra are not superimposable.

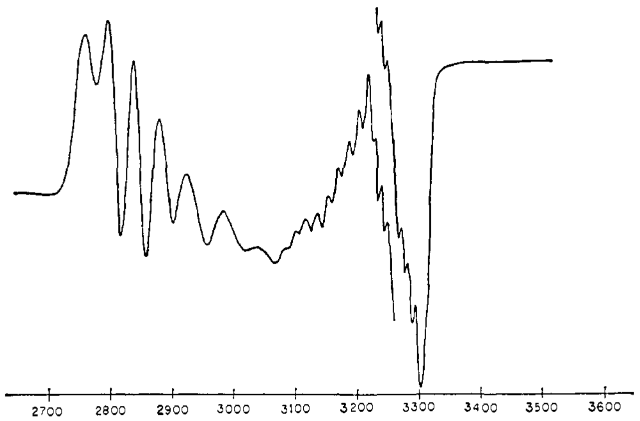

Figure 5. Esr spectrum of 0.005 *M* Co(p-OCH$_3$)TPP in a toluene–piperidine glass in the presence of air (the base line was adjusted to place the spectrum of the oxygen adduct on scale); ν = 9132 MHz, field in gauss. The change in the spectrum is reversible.

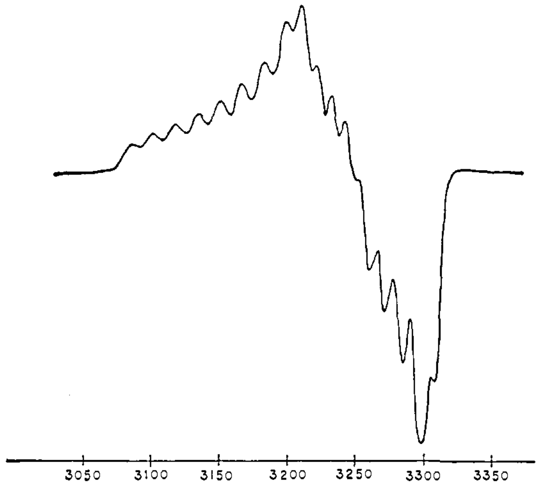

Figure 6. Esr spectrum of 0.005 *M* Co(p-OCH)TPP in toluene containing 0.612 *M* pyridine and oxygen; ν = 9125 MHz, field in gauss.

taining quinuclidine (1,4-ethylenepiperidine), which clearly showed parallel lines split into five components which had intensity ratios of approximately 1:2:3:2:1 (see Figure 4b) with the perpendicular lines compressed into one broad absorption envelope.

None of the samples studied was affected by the presence of a molar excess of metal-free porphyrin, as were the spectra of a number of copper porphyrins in pyridine and other solvents.[13]

Co(p-OCH$_3$)TPP in Toluene–Amine Glasses in the Presence of Air. Figure 5 shows the spectrum of Co(p-OCH$_3$)TPP in piperidine–toluene glasses in the presence of air. The sharp spectrum in the center of Figure 5 was no longer present when the sample tube was evacuated and sealed, and reappeared when the tube was again opened to the air. This spectrum, shown in more detail in Figure 6, is attributed to a complex of Co(p-OCH$_3$)TPP with one amine and one oxygen molecule as the fifth and sixth ligands, since it did not exist when either amine or oxygen were absent. It is similar in all respects to that reported by Bayston, King, Looney, and Winfield[6] for vitamin B$_{12r}$ in the presence of oxygen, except that it shows slightly better resolution. It is also similar to that reported recently by Hoffman, *et al.*,[12] for Co(acac)$_2$en·amine·O$_2$, except that the latter compound shows a more complex esr spectrum due to a small rhombic distortion of the perpendicular branch. The intensity of this spectrum relative to that of the 2:1 (or 1:1 in more dilute solutions) amine complex spectrum is a function of amine concentration and oxygen pressure.[17] In 0.0621 *M* pyridine with an oxygen pressure of 1 atm only the spectrum shown in Figure 6 was observed, and the intensity of this spectrum remained constant over more than 3 months, indicating that no irreversible oxidation of cobalt took place over this period of time, even though the sample was stored at room temperature.

Two different types of esr spectra were also observed for Co(p-OCH$_3$)TPP in pure toluene glasses in the presence of different pressures of air. The splitting constants and *g* values are similar to those for the amine + oxygen complexes.[17] Because of the very small splitting constants observed for Co(p-OCH$_3$)TPP in the presence of oxygen and the fact that $g_{\parallel}$ and $g_{\perp}$ are close to the free-electron value, it would seem unlikely that any of the additional sets of lines observed in polycrystalline samples after a long period of time (see above) could be due to an oxygen adduct. However, when Co(p-OCH$_3$)TPP was crystallized from piperidine solution the polycrystalline sample showed three overlapping esr spectra: that of polycrystalline Co(p-OCH$_3$)TPP as discussed above, that of the monopiperidine adduct, and that of the six-coordinate piperidine–O$_2$ adduct. Observation of an oxygen adduct of the monopiperidine complex in a polycrystalline state is in agreement with the fact that polycrystalline samples of vitamin B$_{12r}$ (where the fifth coordination site is filled by imidazole) have been found to add oxygen to the sixth position.[6]

Discussion

The data of Table I point out several interesting and unexpected facts. The most obvious is the absence of any definite correlation between esr parameters and the basicity of the amine. For example, pyrrole and piperidine are, respectively, the least and most basic amines studied, and yet their 1:1 complexes with Co(p-OCH$_3$)TPP show similar g values and splitting constants. Within the aromatic amines (excluding those having possible steric interactions) there appears to be a small trend, with a decrease in the parallel splitting constant and an increase in the N shf splitting constant as the basicity of the amine increases, but the variations observed are small. The basicity of the amine, however, does play a definite role in the formation of the 2:1 adduct, as evidenced by the fact that weaker bases (pyrrole and quinoline) and those involving possible steric interference with coordination (2-picoline, collidine, and quinoline)[18] did not form 2:1 complexes in 50–90% amine solvent composition, whereas the strongest bases (quinuclidine, piperidine, and n-hexylamine) formed such strong 2:1 complexes that it was necessary to have a large molar excess of solid Co(p-OCH$_3$)TPP in order to observe the esr spectrum of the 1:1 adduct.[19] N-Methylimidazole, which is more basic than the substituted pyridines (pK_a = 7.06 at 25° as compared with the pK_a for 3,4-lutidine = 6.46[20]) and thus a better σ donor, does not form a 2:1 amine complex with Co(p-OCH$_3$)TPP, although its 1:1 complex shows more delocalization onto the amine ($A_{\|\mathrm{Co}}$ is smaller, A_N is larger). This suggests that there may be other factors in addition to ligand basicity influencing complex formation, and that the ability of a given amine to form a 2:1 complex with Co(p-OCH$_3$)TPP may involve a sensitive balance between the σ-donating and π-accepting ability of the amine. Imidazoles are known[21,22] to form weaker complexes than pyridines in cases where the metal ion has π-donating rather than π-accepting capabilities, and the results of comparative studies of bipyridyl and 4,2′-pyridylimidazole have been interpreted in terms of imidazole being a poorer π acceptor than pyridine.[22] The same sort of esr behavior as that described above has been observed for factor B$_r$ and Co(Dmg)$_2$,[4] where pyridine forms 2:1 adducts while imidazole does not, although the structure of the 2:1 amine–Co complex spectrum is considerably different in these cases than in the present study.

The esr parameters for the 2:1 adducts do not show any definite correlation with amine basicity or ability to π bond within experimental error, but those of the oxygen complexes with aromatic amines show a small decrease in both parallel and perpendicular splitting constants as the basicity of the amine increases. It was also noted that the *ease of formation* of the oxygen adduct was a function of amine basicity; relatively high pressures of air were required to form the O$_2$–pyrrole complex, whereas there was difficulty in *removing* all of the O$_2$ adduct when piperidine or n-hexylamine was present.

The effects of substitution on the phenyl rings of the porphyrin on the esr parameters for the 1:1 pyridine–CoTPP complex and its O$_2$ adduct are shown in Table II. It appears that very small substituent effects are present, with the more electron-donating substituents producing larger splitting constants (and larger N shf splittings for the five-coordinate complexes), but the magnitude of these effects is only slightly greater than experimental error. It is reasonable that these effects are very small, since numerous crystal structures of tetraphenylporphyrins have shown that the phenyl rings are at nearly right angles to the plane of the porphine nucleus[23] and thus cannot be expected to allow π delocalization from the phenyl rings to the porphine nucleus.

The Co–O$_2$ adducts discussed here are closely related to others whose kinetic behavior has been studied earlier[24–26] except that in the present system a stable amine–Co–O$_2$ adduct can be preserved over long periods of time in the presence of 1 atm of O$_2$. Preliminary studies[17] of the reaction

$$\mathrm{Co}(p\text{-OCH}_3)\mathrm{TPP}\cdot\text{amine} + \mathrm{O}_2 \rightleftarrows \mathrm{Co}(p\text{-OCH}_3)\mathrm{TPP}\cdot\text{amine}\cdot\mathrm{O}_2 \quad \text{(I)}$$

in toluene indicate that the rate of the forward reaction is much slower than oxygenation reactions involving Co(histidine)$_2$,[24] Co(NH$_3$)$_5$$^{2+}$,[25] or Co(CN)$_5$$^{3-}$.[26] If solutions containing a mixture of Co(p-OCH$_3$)TPP·amine and its oxygen adduct were allowed to stand for long periods of time, the intensity of the two overlapping esr signals decreased slowly, probably due to

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[18] The fact that 2-picoline and collidine form even 1:1 complexes with Co(p-OCH$_3$)TPP is somewhat surprising, and indicates that the cobalt atom is probably out of the plane of the porphyrin nitrogens in the five-coordinate complexes. (See ref 23 a, b, e, g for reports of similar five-coordinate complexes.) It is then not unreasonable that the second amine cannot be added, since the cobalt could then not relieve all steric strains by moving out of the plane of the porphyrin nitrogens.

[19] This experimental fact can be explained in terms of the relative solubilities of the four-, five-, and six-coordinate complexes. The solubility of Co(p-OCH$_3$)TPP in toluene at room temperature is 2.2×10^{-4} M, whereas the 1:1 amine adduct is approximately 20 times more soluble and the 2:1 amine adduct is considerably more soluble than the 1:1 adduct. If aliphatic amine solutions of about 1×10^{-3} M were prepared in toluene in the presence of a large excess of solid Co(p-OCH$_3$)TPP, the equilibrium conditions were such that the major species present in solution was the 1:1 amine adduct, with the four-coordinate compound too dilute (or of too low signal amplitude, since then the spectrum is spread over more than twice the field range of that for the five-coordinate complex) to be observed under these conditions.

[20] L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

[21] L. M. Epstein, D. K. Straub, and C. Maricondi, *Inorg. Chem.*, **6**, 1720 (1967).

[22] W. J. Eilbeck, F. Holmes, G. G. Philips, and A. E. Underhill, *J. Chem. Soc. A*, 1161 (1967); F. Holmes, K. M. Jones, and E. G. Torrible, *ibid.*, 4790 (1961).

[23] (a) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Amer. Chem. Soc.*, **89**, 1992 (1967); (b) M. D. Glick, C. H. Cohen, and J. L. Hoard, *ibid.*, **89**, 1996 (1967); (c) E. B. Fleischer, C. K. Miller, and L. E. Webb, *ibid.*, **86**, 2342 (1964); (d) S. Silvers and A. Tulinsky, *ibid.*, **86**, 927 (1964); (e) D. M. Collins and J. L. Hoard, *ibid.*, **92**, 3761 (1970); (f) R. Countryman, D. M. Collins, and J. L. Hoard, *ibid.*, **91**, 5166 (1969); (g) R. Timkovich and A. Tulinsky, *ibid.*, **91**, 4430 (1969).

[24] J. Simplicio and R. G. Wilkins, *ibid.*, **89**, 6092 (1967).

[25] J. Simplicio and R. G. Wilkins, *ibid.*, **91**, 1325 (1969).

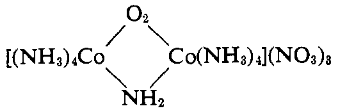
[26] J. H. Bayston, F. D. Looney, and M. E. Winfield, *Proc. Int. Conf. Coord. Chem., 12th*, 80 (1969).

formation of the peroxo binuclear cobalt complex as in all of the above-mentioned systems.[24-27]

$$\mathrm{Co(}p\text{-}\mathrm{OCH_3)TPP\cdot amine + Co(}p\text{-}\mathrm{OCH_3)TPP\cdot amine\cdot O_2 \rightleftarrows amine\cdot Co(}p\text{-}\mathrm{OCH_3)TPP{-}O_2{-}Co(}p\text{-}\mathrm{OCH_3)TPP\cdot amine} \qquad \text{(II)}$$

This binuclear complex should be diamagnetic, which would account for the loss of esr signal. The signal was restored to its original total intensity by either heating the sample or by pumping off the oxygen. Thus it appears from the esr behavior that both reactions I and II are reversible, in agreement with the fact that the formation of some other peroxo binuclear cobalt complexes has been found to be reversible.[24,25,27]

One-electron oxidation of several bridged dicobalt peroxo species has been reported.[28] The solution esr spectra of compounds such as $K_5[(CN)_5CoO_2Co(CN)_5]$ and $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$ show that the electron is shared equally by the two cobalt atoms and that the electron is mainly localized on the oxygen. The esr parameters calculated from the 15-line spectra of the two complexes ($g_0 = 2.0200$, $a_0 = 0.000803$ cm^{-1}; $g_0 = 2.0249$, $a_0 = 0.00108$ cm^{-1}, respectively) are similar to those observed for Co(p-OCH$_3$)TPP·amine·O$_2$ in this work (pyridine $g_0 = 2.027$, $a_0 = 0.00127$ cm^{-1}; 3,4-lutidine $g_0 = 2.025$, $a_0 = 0.00117$ cm^{-1}; n-hexylamine $g_0 = 2.027$, $a_0 = 0.00120$ cm^{-1}). Weil and Kinnaird[29] have also studied the compound



$$[(NH_3)_4Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(NH_3)_4](NO_3)_3$$

which shows the same type of esr spectrum as the singly bridged peroxo species discussed above. When the bridging oxygen was enriched with ^{17}O the esr spectrum showed a large oxygen hyperfine splitting ($a_{0_0} = 0.00214$ cm^{-1}, $a_{0_{Co}} = 0.00118$ cm^{-1}, $g_0 = 2.0341$). Qualitative calculations show that the peroxo bridge is best described as a modified superoxide ion.[29] The similarity of the esr parameters of these binuclear complexes to the mononuclear Co–O$_2$ complexes of vitamin B$_{12r}$,[6] Co(acac)$_2$en,[12] and Co(p-OCH$_3$)TPP indicates that they all have very similar electronic configurations. The mononuclear complexes reported earlier[6,12] have thus been formulated as Co(III)–O$_2^-$ complexes, where the oxygen exists formally as a superoxide ion, as in the above dibridged complex of Weil and Kinnaird.[29] It seems reasonable, as previously suggested by others,[12,29,30] that the electron has been transferred from the d_{z^2} orbital of cobalt to a $2p\pi^*$ orbital of the oxygen molecule, where the degeneracy of the two $2p\pi^*$ orbitals has been split by bond formation with the cobalt.

The difficulty encountered in removing all of the oxygen from solutions of Co(p-OCH$_3$)TPP in the presence of piperidine and n-hexylamine, mentioned earlier in the discussion, may now be understood in terms of the electronic configuration discussed above: coordination of very basic amines should facilitate electron transfer to the oxygen, which should lead to stronger bond formation between cobalt and oxygen.

The oxygen adducts studied here show very similar esr spectra to those for dimethyl sulfoxide solutions of Na$_4$CoPTS (PTS = phthalocyanine tetrasulfonate) which have undergone two-electron reduction.[31] The authors[31] mention the odor of dimethyl sulfide and suggest the oxidation of the postulated Co(0) phthalocyanine to Co(I) or Co(II). It seems quite possible that the species whose esr spectrum was observed ($g_{\parallel} = 2.13$, $g_{\perp} = 2.02$, $A_{\parallel} = 0.006$ (estimated), $A_{\perp} = 0.0017$ cm^{-1}) was a CoPTS(DMSO)(O$_2$)$^{4-}$ complex derived from Co(II) rather than a Co(0) species, and the observed hyperfine splittings were due to Co rather than N as suggested by the authors.[31] This would explain the observed difficulty in reproducing the spectrum, since the amount of O$_2$ produced by oxidation of solvent after each polarographic reduction of CoPTS^{4-} probably varied with the time and actual techniques involved in observing the esr spectrum.

Another interesting feature of this system is the sensitivity of the esr spectrum to the quality of the glass. Assour[3] was apparently able to observe well-resolved spectra of Co(pc) in amine solvents such as pyridine, 4-picoline, and quinoline, whereas in the present study, where the parallel and perpendicular branches of the 2:1 amine complex spectra strongly overlapped, this was not possible. Studies showing variations in the resolution of esr spectra in frozen aqueous solutions have been reported by Ross,[32] who points out that if the solvent crystallizes, the solute will be segregated. This concentration of paramagnetic species will result in dipolar broadening of the esr spectrum. If the solution can be frozen rapidly enough to prevent diffusion of solute molecules, then good glasses can be obtained. The most rapid method is plunging the sample into liquid nitrogen, but even then the time involved is 1–2 sec. This is sufficiently fast to prevent both solute aggregation and solution crystallization which might trap solute molecules in a less than random fashion (a) if the viscosity of the solvent is great enough, (b) if the solvent does not tend to crystallize easily, or (c) if the rate of crystal growth is slow.[32] The difficulty encountered in observing the spectrum of Co(p-OCH$_3$)TPP in toluene glasses may be interpreted in terms of these problems. As mentioned above, the spectrum of polycrystalline Co(p-OCH$_3$)TPP was always observed, and if the sample was warmed and then refrozen slowly the glass spectrum disappeared. Under conditions of slow cooling the toluene may be able to crystallize, causing further aggregation of the solute to the point where only the polycrystalline species is present.

It seems reasonable in retrospect, when one considers molecular shapes and symmetries, melting points, and viscosities, that toluene, o- and m-xylene, α-bromonaphthalene, chlorobenzene, and diphenyl ether were found to produce good spectral resolution (Table III), whereas benzene, pyridine, and p-xylene produced very poor spectral resolution of the most sensitive spectrum, that of the 2:1 amine complex. However, without extensive thermodynamic, crystallographic, and physical data it would be difficult to predict whether a given

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(27) It appears, however, that the formation of $[(CN)_5Co{-}O{-}Co(CN)_5]^{6-}$ is not reversible along the pathway indicated by eq II, but requires additional O$_2$ to be returned to the mononuclear species $[(CN)_5Co{-}O_2]^-$.[26]

(28) M. Mori, J. A. Weil, and J. K. Kinnaird, *J. Phys. Chem.*, **71**, 103 (1967).

(29) J. A. Weil and J. K. Kinnaird, *ibid.*, **71**, 3341 (1967).

(30) M. Mori and J. A. Weil, *J. Amer. Chem. Soc.*, **89**, 3732 (1967).

(31) L. D. Rollmann and R. T. Iwamoto, *ibid.*, **90**, 1455 (1968).

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solvent (dioxane, for example) would produce good glasses. It would seem wise to compare several possible solvents when the resolution of a particular spectrum is in question.

The perpendicular branch of the esr spectrum of the 2:1 complex is markedly different in the present study than that of Co(pc) in the presence of various amines.[3] The only spectrum of a 2:1 adduct which was similar to those observed by Assour[3] was that of the quinuclidine adduct. This may indicate that this six-coordinate complex (and possibly also those of Co(pc)[3]) is distorted from octahedral symmetry, possibly causing one amine–cobalt bond to be longer than the other, or pushing the cobalt ion out of the plane of the porphyrin ring as it probably is in the five-coordinate complexes.[23a,b,e,g] Such distortions have been observed in metal porphyrins; for example, see ref 23f for an interesting report on the crystal structure of the low-spin Fe(III) complex FeTPP(imidazole)$_2$$^+Cl^-$, which shows distinctly different bond lengths for the two imidazole N–Fe bonds, and a slight displacement of Fe from the plane of the porphyrin nitrogens.

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Electron Delocalization and Bonding in Some Paramagnetic Bisarene Complexes. I. Nuclear Magnetic Resonance Contact Shift Studies

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Abstract: The nuclear magnetic resonance contact shifts have been observed for a large number of paramagnetic bisbenzene and methyl-substituted bisbenzene complexes of first row transition metals. Electron delocalization was rationalized consistently on the basis of competing direct σ and indirect π delocalization mechanisms, the π mechanism becoming dominant in traversing the transition series from left to right. Pseudocontact shifts were estimated for D$_{6h}$ and C$_{2v}$ symmetries, and found to be negligible in all cases studied except possibly for the bishexamethylbenzeneiron(I) cation. The anomalous upfield methyl resonance shifts for Cr(I) and V(0) methyl-substituted complexes have been explained in terms of a strong polarization of the filled, predominantly metal e$_{2g}$ MO's by the unpaired spin in the a$_{1g}$ MO. Contrary to proposals which place the highest energy electrons in ring antibonding orbitals, in the complexes reported here as in most of the metallocenes, the highest energy electrons are placed in molecular orbitals which are largely metal ion and whose energy ordering is precisely that predicted by ligand-field theory: $d_{x^2-y^2}, d_{xy} < d_{z^2} \ll d_{xy}, d_{yz}$.

The recent nmr contact shift studies of the metallocenes by Rettig and Drago,[2,3] which recognized the importance of the σ orbitals of the ligand in delocalization of spin density, prompted our investigation of the contact shifts of a large number of paramagnetic bisarene complexes. Preliminary results for Cr(C$_6$H$_6$)$_2$$^+$ and V(C$_6$H$_6$)$_2$ have been reported.[4] The dominance of σ delocalization has been demonstrated for these species and a detailed analysis of the value of ψ^2 at the ring protons has shown that a "direct interaction" between the metal orbitals and the hydrogen 1s orbital, recently postulated by several workers,[5,6] makes only a small contribution to this extensive σ delocalization. Subsequent qualitative work by Prins[7] has reached essentially the same conclusions as Rettig and Drago[3] concerning delocalization in the metallocenes.

The nature of electron delocalization in the analogous benzene complexes, while having been the subject of several epr,[8–13] nmr,[6] and theoretical[7,13,14] studies, has

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