Table I. Raman Spectra of Metal Complexes of Diphenyldithiophosphinic Acid

$Ni[S_2PPh_2]_2$					$Cr[S_2PPh_2]_3$					
Solid		CS_2 soln			Solid		CS_2 soln			
$\Delta\nu$, cm^{-1}	Intens[a]	$\Delta\nu$, cm^{-1}	Intens[a]	ρ_1[b]	$\Delta\nu$, cm^{-1}	Intens[a]	$\Delta\nu$, cm^{-1}	Intens[a]	ρ_1[b]	Assignment
124	ms									
223	w				227 ± 4	w				
244	w				247 ± 4	sh				
258	ms									
295	s	286	s	0.27	290	s	282	vs	p	Sym ν_{M-S}
368	m	366[c]	vw	p	365	m				
586	m	585[c]	w	p	580	m				ν_{P-S}?[d]
610	w									
632	w									
1007	ms	1001	m	0.06	1007	ms	999	s	0.06	ν_{C-C} and δ_{HCC}
1035	w	1030	w	0.01	1035	vw	1029	mw		
1107	m	1103	mw	0.05	1109	m	1101	m	0.16	
1593	m	1591	vw	dp?	1593	m	1588	w	dp?	ν_{C-C}
3063	m	3060	mw	p	3063	m	3059	m	p	ν_{C-H}

[a] s, m, w, v, and sh stand for strong, medium, weak, very, and shoulder, respectively. Intensities for 4880-Å excitation. [b] Depolarization ratios where quoted are accurate to ±10% and are for 4880-Å excitation. All strong and medium-intensity bands showed similar depolarization ratios with the other three excitation lines used in this work. [c] CH_2Cl_2 solution. [d] Infrared data; see ref 3 and 4.

intensity of the four bands at 282, 999, 1029, and 1101 cm^{-1} in the Raman spectra of $Cr[S_2PPh_2]_3$ solution are plotted as a function of excitation frequency in Figure 1. These intensities were obtained using the 800-cm^{-1} doublet of CS_2 as the internal standard and were corrected for the instrumental response.[9]

The intensity of the polarized band at 282 cm^{-1} in the solution spectra of $Cr[S_2PPh_2]_3$ shows strong resonance enhancement as the exciting line frequency moves toward the high-frequency region. Its intensity at 4579 Å is about four times greater than that observed with 5145-Å excitation, Figure 1. The intensity of this Raman band is mainly enhanced by the uv absorption band(s) and not by the visible absorption band (centered at about 5700 Å) as the Raman band has greater intensity with 4880-Å excitation than with 5145-Å excitation although the latter wavelength occurs in the region of greater absorption of 5700-Å band, Figure 1. Cavell et al.[3,4] have suggested that the absorption in the visible region is caused by d–d transitions of Cr(III) and that the uv absorption bands are charge transfer and intraligand in origin. The Raman band at 282 cm^{-1} is assigned to symmetric Cr–S stretching vibration, Table I, as such a vibration is expected to be resonance enhanced by the charge-transfer absorption. The bands at 1029 and 1101 cm^{-1} show very small intensity enhancement with the decrease in the wavelength of the exciting radiation. These two bands and the one at 999 cm^{-1} most probably arise from the vibrations of the phenyl groups and hence are expected to show resonance enhancement only when the excitation frequency is in or close to the intraligand bands which are expected to occur at much higher frequencies than the ones used here.[10] The horizontally aligned bands in Table I show similar dependence of their intensities on the excitation frequency for both compounds. The bands above 900 cm^{-1} are very similar in nature and it seems reasonable to associate them with the phenyl rings in both complexes.

Raman spectra of $Ni[S_2P(OEt)_2]_2$ in CS_2 solution showed only one strong polarized band at 309 cm^{-1} having $\rho_l = 0.2 \pm 0.03$ with 4880-Å excitation. No feature was observed above the 900-cm^{-1} region under the conditions similar to those used for $Ni[S_2PPh_2]_2$ and $Cr[S_2PPh_2]_3$. This again supports the assignment of the features above 900 cm^{-1} in phenyl derivatives to the vibrations of the phenyl groups, Table I. The band at 309 cm^{-1} in $Ni[S_2P(OEt)_2]_2$ is strong and polarized and has an excitation profile (intensity vs. excitation frequency plot) very similar to that seen for the 286-cm^{-1} band in the solution spectrum of $Ni[S_2PPh_2]_2$. Therefore it is believed that it also arises mainly from the symmetric Ni–S stretching vibrations. Thus the symmetric Ni–S stretch increases by ~23 cm^{-1} in $Ni[S_2PX_2]_2$ complexes where X = Ph is replaced by X = OEt. This is in agreement with the results obtained from the infrared spectra of these complexes.[4] The increase in frequency on replacement of phenyl groups by ethoxy groups is consistent with the fact that the Ni–S bond is slightly shorter in ethoxy compounds than in compounds with phenyl groups.[4]

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Registry No. $Ni[S_2P(OEt)_2]_2$, 16743-23-0; $Ni[S_2PPh_2]_2$, 22239-85-6; $Cr[S_2PPh_2]_3$, 14871-17-1.

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Stepwise Formation of Macrocyclic Ligands Containing Nitrogen Donors

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The importance of metal complexes containing synthetic macrocyclic ligands as models for a variety of biochemical processes is now well recognized. However, although there

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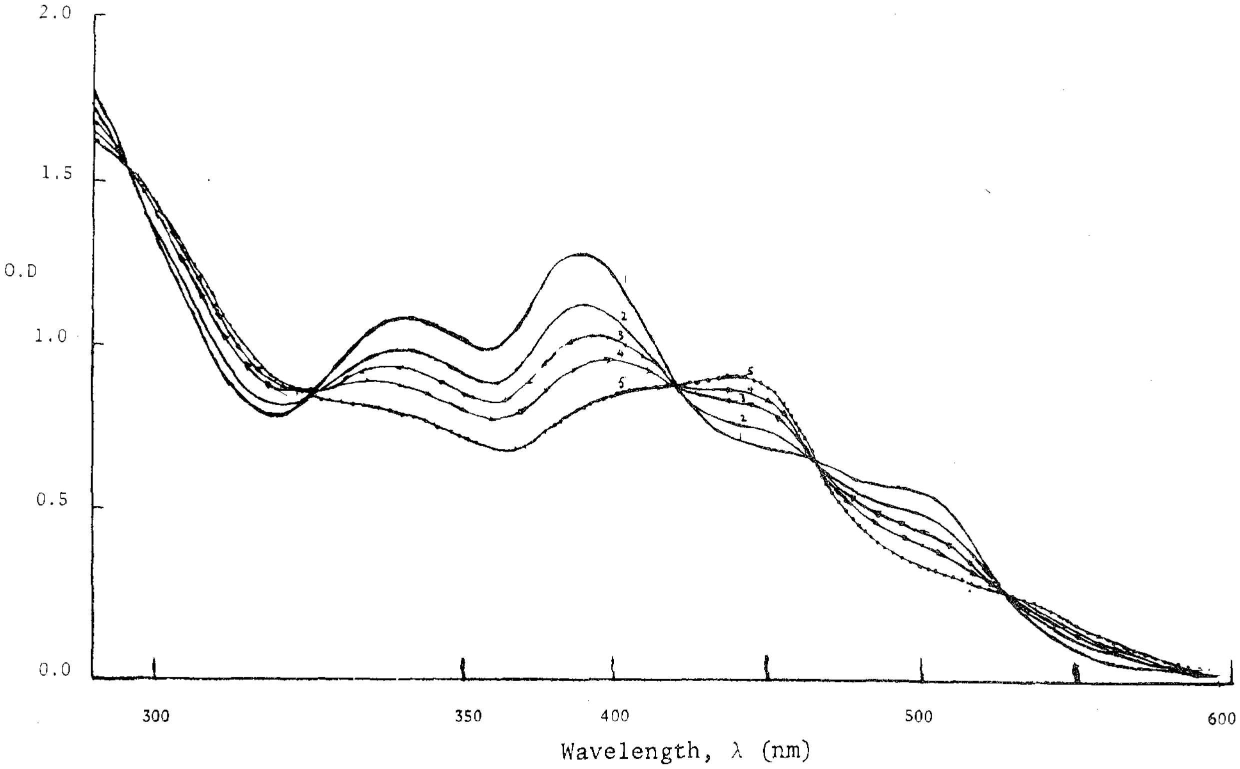
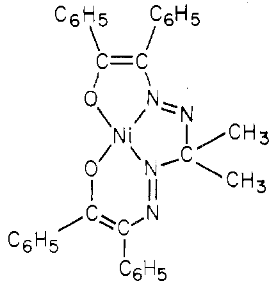


Figure 1. Visible spectra obtained during the reaction of NiMMK with 1,3-propanediamine in tetrahydrofuran at 66°.

is an abundance of reported data concerning the synthesis, characterization, and reactions of macrocyclic complexes, there is little available information on the mechanisms by which the ligands are formed in "template" reactions. Blinn and Busch[1] have reported spectral changes and some data for the kinetics of ring closure of 2,3-pentanedionebis(mercaptoethylimino)nickel(II) with α,α'-dibromo-*o*-xylene. No studies relating to kinetics and mechanism of formation of macrocyclic ligands with an N_4 donor set have been reported.

We have described condensation reactions between a nickel(II) complex containing a tetradentate ligand with an N_2O_2 donor set derived from benzil monohydrazone, I (abbreviated NiMMK), and some amines in the absence of a solvent. With ethylenediamine and 1,2-propanediamine, complexes containing macrocyclic ligands were obtained, although with 1,3-propanediamine the complex obtained (abbreviated NiApSo[3]) contains a noncyclic ligand in which only one of the coordinated CO groups has undergone reaction. These reactions provide an ideal opportunity to follow the formation of a macrocyclic ligand with an N_4 donor set via a ring-closure process since the mode of coordination of the ligand in the low-spin square-planar complex NiMMK results in cis orientation of the reactive CO groups.[4,5]



I

Results and Discussion

Reactions between NiMMK, I, and the amines ethylenediamine and 1,3-propanediamine have been followed spectrophotometrically in tetrahydrofuran at its boiling point (66°). Pseudo-first-order conditions were established for the reactions by using NiMMK concentrations of (2–8) × 10^{-3} *M* and amine concentrations of 0.3–0.8 *M*. Samples were removed from the solution under investigation at various times and injected into tetrahydrofuran at room temperature such that the final concentration of complex was 8 × 10^{-5} *M*. Spectra were then recorded from 600 to 275 nm (Unicam SP 800B and Beckman DU spectrophotometers) in a 1-cm path length cell.

Figure 1 shows a series of spectra obtained during the reaction of NiMMK with 1,3-propanediamine. The observation of several well-defined isosbestic points supports the presence of only two uniquely absorbing species in solution and the absence of considerable concentrations of reaction intermediates. The two species correspond to NiMMK (spectrum 1) and NiApSo (spectrum 5) at the beginning and end of the reaction, respectively. (These spectra are identical with those reported earlier.[2,6]) The spectra obtained for the reaction of NiMMK with ethylenediamine are shown in Figure 2. It is apparent that there are more than two uniquely absorbing species in the formation of the macrocyclic complex NiHcyclo-13[3] (spectrum 8). At 360 nm, the optical density of the solution initially falls and then remains constant whereas, in the region of 340 nm, an initial drop in optical density is followed by a subsequent increase. Spectrum 5 in this series is similar to that of NiApSo and also to the product of the reaction between NiMMK and *unsym*-dimethylethylenediamine in which only one of the coordinated CO groups has undergone condensation. It is thus apparent that the formation of the macrocyclic complex NiHcyclo-13 occurs via a two-step process with the rates of the two steps being comparable. The two steps correspond to successive reactions of the two coordinated CO groups of NiMMK with one molecule of ethylenediamine. Since the rates of the two steps are comparable, a significant concentration of an intermediate in which only one coordinated CO group has condensed with one end of the ethylenediamine builds up during the reaction. The presence of the intermediate has been confirmed by the addition

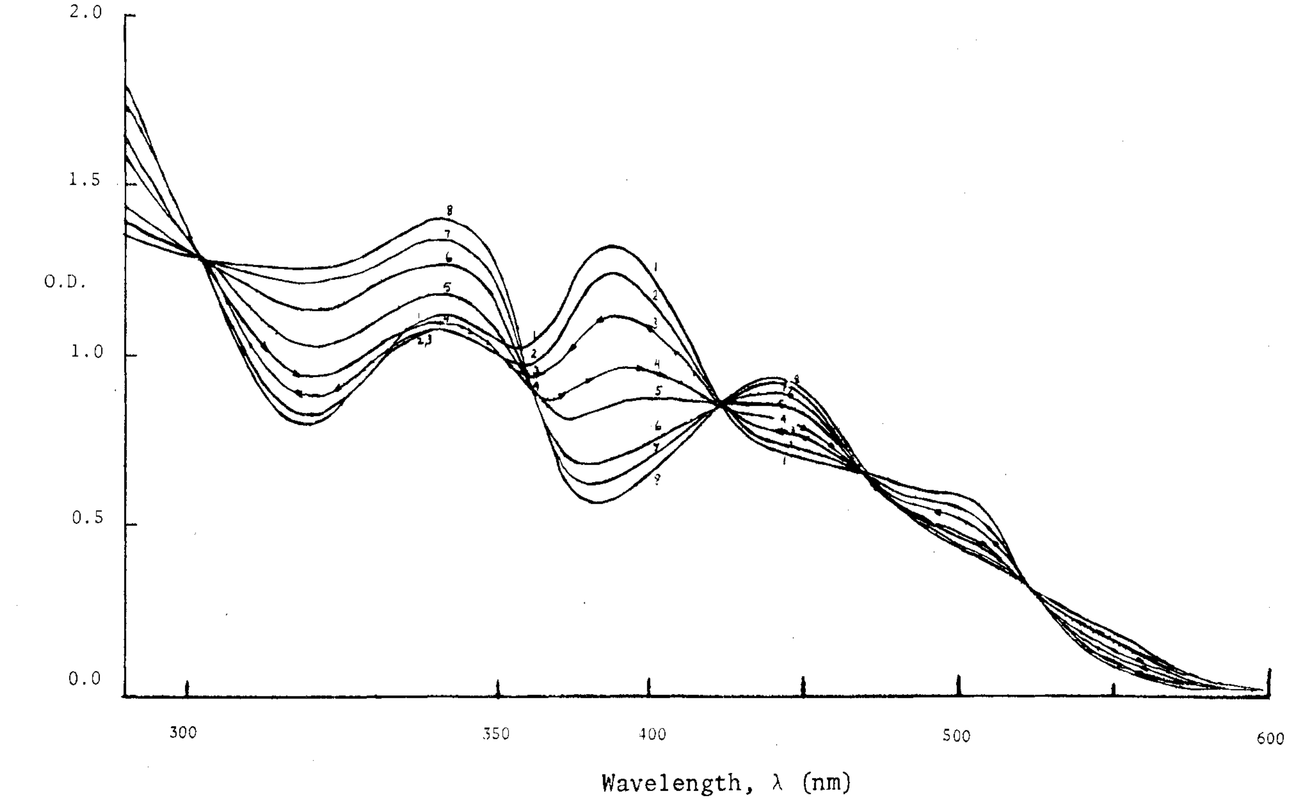


Figure 2. Visible spectra obtained during the reaction of NiMMK with ethylenediamine in tetrahydrofuran at 66°.

of benzoyl chloride to the reaction medium when the visible spectrum corresponds to that of no. 5 in Figure 2. A mass spectrum of the resulting precipitate shows the presence of a monobenzoylated derivative of the proposed intermediate. (NiApSo also reacts with benzoyl chloride and *p*-toluenesulfonyl chloride in a similar manner.[2]) Blinn and Busch[1] did not detect any buildup of an intermediate in the reaction of 2,3-pentanedionebis(mercaptoethylimino)nickel(II) with α,α'-dibromo-*o*-xylene. Although a two-step mechanism was proposed for the formation of the macrocycle, it was concluded that after reaction of the first mercapto group, the orientation of the sulfur and halide is such that the second (cyclization) step is very rapid. The relatively slow second step observed for the reaction of NiMMK with ethylenediamine is probably the result of two effects. First, the amine remains flexible after the first condensation and thus the "kinetic coordination template effect"[1] is not as effective as in the reaction described by Blinn and Busch and, second, the reactivity of the coordinated CO groups in NiMMK is different,[2] this arising because one is part of a five-membered chelate ring whereas the other is part of a six-membered chelate ring.[5]

It has been possible to obtain some preliminary data on the kinetics and mechanism of the reactions of NiMMK with 1,3-propanediamine (pn) and ethylenediamine (en) by selecting wavelengths where suitable optical density changes occur. The rate of formation of NiApSo (measured at 340 and 385 nm) is dependent on [NiMMK] and [pn] although with hydroxide ion the dependence is first order at low concentrations ((0–2) $\times 10^{-3}$ *M*) and independent at higher concentrations ($>8 \times 10^{-3}$ *M*). This behavior is consistent with a mechanism in which a change in rate-determining step occurs as the [OH$^-$] changes. If we propose a mechanism involving a preequilibrium followed by base-catalyzed elimination of water such as

$$\text{NiMMK} + \text{pn} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{NiMMK·pn} \qquad (1)$$

$$\text{NiMMK·pn} \xrightarrow{k_2[\text{OH}^-]} \text{NiApSo} + \text{H}_2\text{O} \qquad (2)$$

then we can write

$$\frac{d[\text{NiApSo}]}{dt} = \frac{k_2K[\text{NiMMK}][\text{pn}][\text{OH}^-]}{1 + \dfrac{k_2}{k_{-1}}[\text{OH}^-]} \qquad (3)$$

where K ($=k_1/k_{-1}$) is the equilibrium constant for the formation of the adduct NiMMK·pn. At low [OH$^-$], eq 3 reduces to

$$d[\text{NiApSo}]/dt = k_2K[\text{NiMMK}][\text{pn}][\text{OH}^-] \qquad (4)$$

and the base-catalyzed elimination of water is the rate-determining step.

At high [OH$^-$] eq 3 becomes

$$d[\text{NiApSo}]/dt = k_1[\text{NiMMK}][\text{pn}] \qquad (5)$$

and the formation of the adduct is now the rate-determining step. By working at high [OH$^-$] where the rate is independent of [OH$^-$] and under pseudo-first-order conditions, i.e., a large excess of pn

$$d[\text{NiApSo}]/dt = k_{\text{obsd}}[\text{NiMMK}] \qquad (6)$$

where $k_{\text{obsd}} = k_1[\text{pn}]$. A plot of k_{obsd} vs. [pn] has enabled k_1 to be determined as $(0.79 \pm 0.07) \times 10^{-2}$ M^{-1} min^{-1} at 66°. In order to obtain k_2, the value of K must be determined. However, since no spectral changes are observed at various wavelengths at "zero time", it has not been possible to obtain this value by spectral measurements. The adduct probably involves the formation of a carbinolamine by attack of the amine at the coordinated CO group rather than coordination of the amine to the nickel ion.

For the reaction of NiMMK with ethylenediamine, both steps have been studied separately, the first at 360 nm and the second at 340 and 380 nm (latter part of overall reaction). For the first step, the rate of formation of the intermediate is dependent on [NiMMK] and [en] and is of variable order (first at low concentrations and independent at higher concentrations) 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, $(2.44 \pm 0.2) \times 10^{-2}\ M^{-1}\ \text{min}^{-1}$. 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 $\sim 1.3 \times 10^{-2}\ \text{min}^{-1}$.

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.

Registry No. NiMMK, 55428-46-1; 1,3-propanediamine, 109-76-2; ethylenediamine, 107-15-3.

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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 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.

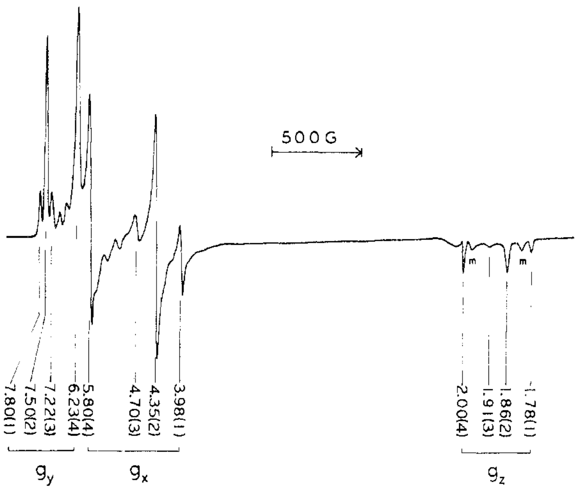

Figure 1. EPR spectrum of the ferric high-spin $TPPH_2(FeCl)$, the mixed crystalline precipitate of $TPPFe^{III}Cl$ and free $TPPH_2$, obtained from acetone and observed at 8°K. The effective g values are indicated for the four species. The peaks designated "m" are tentatively assigned to the transition in the middle Kramers doublet.[18]

Materials and Procedures

$TPPFe^{III}Cl$ was synthesized in dimethylformamide[9] and purified by a dry Al_2O_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. $TPPFe^{III}CH_3COO$ 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]

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

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

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

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