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have inevitably decreased the resolution for the fragment ions.

Chlorophyll *b*, pheophytin *a*, pyrochlorophyll *a*, and the pyrochlorophyll *a* synthetic linked pair[8] all exhibit this intense fragmentation structure, and there is evidence that cyanocobalamin[9,10] also shows the same remarkable fragmentation behavior.

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Infrared Spectroscopy of Oxidized Metalloporphyrins: Detection of a Band Diagnostic of Porphyrin-Centered Oxidation

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A long-standing problem in the redox chemistry of metalloporphyrins is identifying whether the site of redox is metal centered or ligand centered. The most argued case is $[FeCl(TPP)]^+$ (TPP = tetraphenylporphyrinate), which for many years has been considered an iron(IV) complex.[1,2] More recently, a strong case has been made for its reformulation as an iron(III) radical cation.[3,4] Traditionally, choosing between metal or ligand oxidation has relied on solution-derived criteria, particularly UV-VIS spectroscopy, EPR spectroscopy, magnetic moment measurements, and electrochemical methods.[5-7] Such criteria are usually reliable for cases where metal oxidation is well separated in potential (> ~300 mV) from porphyrin ring oxidation but frequently lead to considerable ambiguity in the most interesting cases, namely, those of iron porphyrins. The importance of iron porphyrins which are oxidized above the ferric state lies in their appearance as intermediates in the hemoproteins peroxidase and catalase[8] and probably also in cytochrome P-450.[9] For example, it is generally accepted that the so-called compound I of horseradish peroxidase (HRP I), which is oxidized 2 equiv above iron(III), is an iron(IV) radical cation and not an iron(V) porphyrin.[10,11] UV-VIS spectroscopy,[10] Mössbauer spectroscopy,[12] and very recently ENDOR spectroscopy[13] have provided convincing support for this assignment. However, for many iron porphyrin complexes and other metalloporphyrins there remains considerable ambiguity over their formulation.

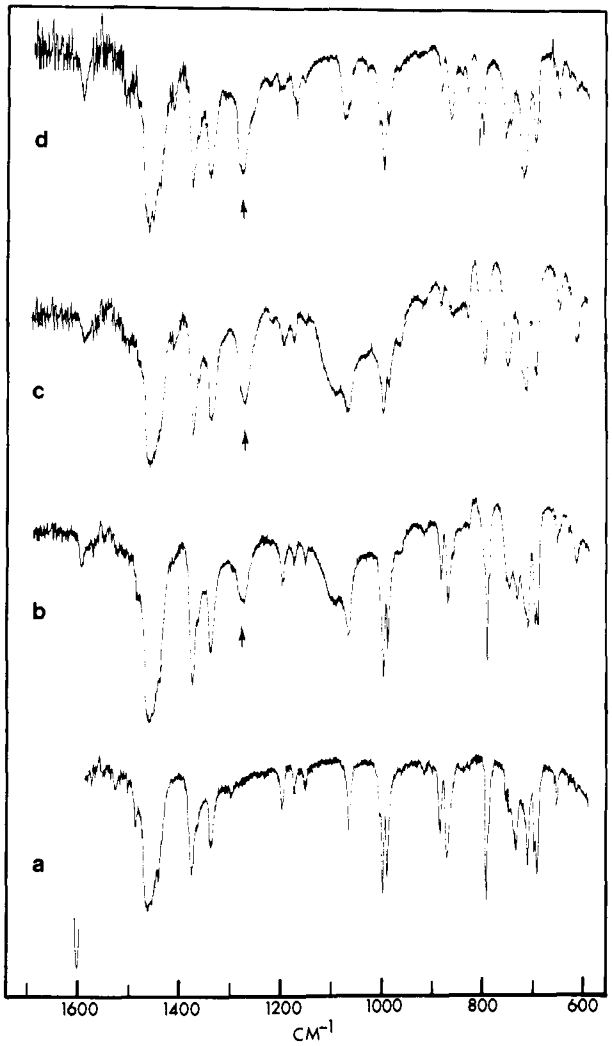

Figure 1. Infrared spectra of μ-oxo dimer iron tetraphenylporphyrin complexes. Compounds were examined as Nujol mulls and spectra were recorded at room temperature by using a single sodium chloride plate. (a) $Fe_2(TPP)_2O$; (b) $[Fe_2(TPP)_2O][ClO_4]$; (c) $[Fe_2(TPP)_2O][ClO_4]_2$; (d) $[Fe_2(TPP)_2O][SbCl_6]_2$.

In the course of our work in developing NMR techniques for characterizing oxidized metalloporphyrins[14,15] and developing preparative methods for their isolation,[3] we have discovered that IR spectroscopy provides a new criterion for identifying porphyrin radical cations. From the numerous cases we have studied, there is reason to believe that this criterion may have a unique generality. It also suggests that distinguishing between metal and ring oxidation in metalloporphyrins has significant chemical implications and is not a question of semantics.

In oxidized tetraphenylporphyrin complexes we find that a strong IR band in the region of 1270-1295 cm^{-1} seems to be diagnostic of the $TPP^{+\cdot}$ radical cation. In Figure 1 are displayed the Nujol mull IR spectra of the μ-oxo ferric dimer $Fe_2(TPP)_2O$ (a), its one-electron oxidation product $[Fe_2(TPP)_2O][ClO_4]$ (b), its two-electron oxidation product as the diperchlorate salt $[Fe_2(TPP)_2O][ClO_4]_2$ (c), and the bis(hexachloroantimonate) salt $[Fe_2(TPP)_2O][SbCl_6]_2$ (d). The perchlorate salts were prepared electrochemically as previously described[14,15] or by silver per-

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Table I. Diagnostic Infrared Bands in Ring-Oxidized Metalloporphyrins[a]

oxidized metalloporphyrin	diagnostic band, cm^{-1}
$[Fe_2(TPP)_2O][ClO_4]$	1270 s
$[Fe_2(TPP)_2O][ClO_4]$ d-8 pyrrole	1254 s
$[Fe_2(TPP)_2O][ClO_4]$ d-20 phenyl	1273 s
$[Fe_2(TPP)_2O][CF_3SO_3]$	1279 vs
$[Fe_2(TPP)_2O][ClO_4]_2$	1270 vs
$[Fe_2(TPP)_2O][SbCl_6]_2$	1285 vs
$[Fe_2(p\text{-}OCH_3TPP)_2O][ClO_4]$	1270 sh
$[Fe_2(p\text{-}OCH_3TPP)_2O][ClO_4]_2$	1284 sh
$[FeCl(TPP)][ClO_4]$	1270 m
$[FeCl(TPP)][SbCl_6]\cdot CH_2Cl_2$[b]	1290 vs
$[Fe(TPP)][ClO_4]_2$[c]	1285 s
$[FeCl(p\text{-}OCH_3TPP)][ClO_4]$	1270 sh
$[MnCl(TPP)][ClO_4]$	1290, 1270 s
$[CrCl(TPP)][SbCl_6]$	1285 vs
$[Cu(TPP)][SbCl_6]$	1295 vs
$[Zn(TPP)][ClO_4]$[d]	1270 vs
$[FeCl(OEP)][ClO_4]$	1540 s
$[Fe(OEP)][ClO_4]_2$	1530 s
$[Fe(OEP)][ClO_4]_2$ d-4 methine	1520 s
$[Fe(OEP)][CF_3SO_3]_2$	1520 m
$[Co(OEP)][Br]_2$[e]	1570 w
$[Co(OEP)][ClO_4]_2$[d]	1554 m
$[Zn(OEP)][CF_3SO_3]$[e]	1535 m

[a] Compounds examined as KBr disks or on single 5-mm NaCl cells as Nujol mulls, uncertainties ±5 cm^{-1}. [b] 1291 cm^{-1} in deuterio-1,1,2,2-dichloroethane solution. [c] The IR spectrum of this compound indicates perchlorate coordination. [d] $^2a_{2u}$ radical type. [e] $^2a_{1u}$ radical type.

chlorate–iodine oxidation.[15] Sample integrity was checked by proton NMR spectroscopy after recording the IR spectrum. The hexachloroantimonate salt was prepared in dichloromethane by using the synthetically convenient phenoxathiin radical cation;[3] sample integrity was checked by UV–VIS spectroscopy following IR measurements. All spectra in Figure 1 have two bands in the region 850–890 cm^{-1} assignable[16] to ν_{Fe-O}. Similar bands in all four compounds strongly supports an intact Fe–O–Fe moiety which is unaffected by the redox reaction. The very small perturbation of the energy of this stretch is consistent with little change in real and/or formal charge at the iron center upon oxidation. Spectra of the three oxidized species (Figure 1b–d) show a strong new absorption near 1270 cm^{-1} which is absent in the parent μ-oxo dimer (Figure 1a). Comparison of the perchlorate and hexachloroantimonate derivatives rules out the possibility that this new band is due to the counterion. Similarly, the trifluoromethanesulfonate salt $[Fe_2(TPP)_2O][CF_3SO_3]$ has a band at 1279 cm^{-1}. Moreover, the same new band is seen in the one-electron and two-electron oxidized μ-oxo ferric dimers of tetra-(p-methoxyphenyl)porphyrin complexes (see Table I). Deuteration studies on the d-20 phenyl singly oxidized dimer showed no significant shift of the diagnostic band. However, deuteration of the pyrrole positions causes a 16-cm^{-1} decrease in the diagnostic band from 1270 to 1254 cm^{-1}. These data indicate that this new band arises from a strongly IR-allowed porphyrin ring mode. Its assignment to a vibrational mode of the $TPP^{+\cdot}$ radical cation is strongly corroborated by the following studies on oxidized monomeric metalloporphyrins.

The zinc species, $Zn(OClO_3)(TPP)$, provides an unambiguous example of a radical cation.[17,18] It has a strong IR band at 1270 cm^{-1} not present in Zn(TPP). Similarly, $[Cu(TPP)][SbCl_6]$ has a strong band at 1295 cm^{-1} not present in Cu(TPP). Figure 2 displays the IR spectra (KBr) for FeCl(TPP) and its one-electron oxidation product isolated as the hexachloroantimonate salt, $[FeCl(TPP)][SbCl_6]\cdot CH_2Cl_2$.[3] The diagnostic band (*) appears at 1290 cm^{-1} only in the radical cation $[FeCl(TPP)][SbCl_6]$.

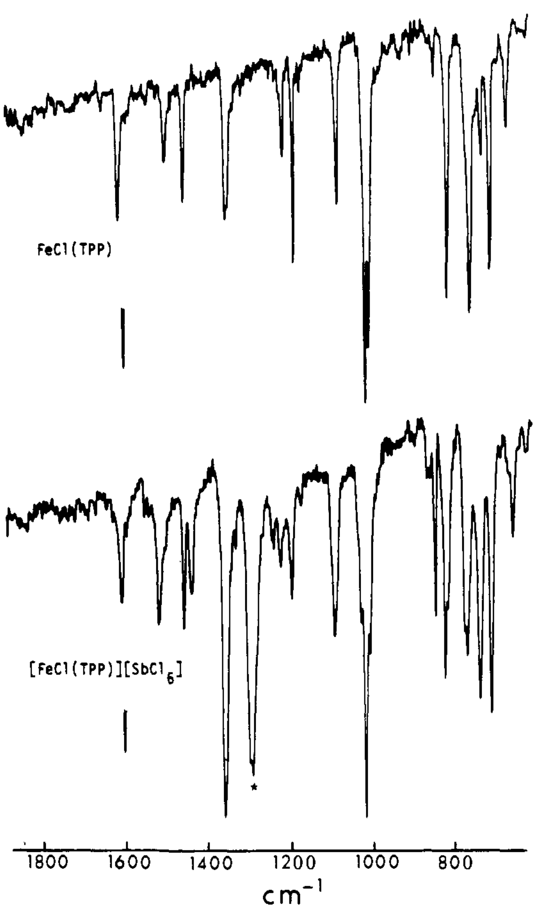

Figure 2. Infrared spectra of monomeric iron tetraphenylporphyrin complexes examined as KBr pellets: FeCl(TPP) (top spectrum); $[FeCl(TPP)][SbCl_6]$ (bottom spectrum). The diagnostic band (*) of the porphyrin radical cation is seen at 1290 cm^{-1}.

Similarly, there is a strong band at 1270 cm^{-1} in the perchlorate salt, $[FeCl(TPP)][ClO_4]$, which is not present in FeCl(TPP) or in $Fe(OClO_3)(TPP)$. Proof that this band does not arise from a solid-state effect comes from its observation in solution. A deuterio-1,1,2,2-tetrachloroethane solution of $[FeCl(TPP)][SbCl_6]$ showed the diagnostic band at 1291 cm^{-1}. Sample integrity was checked in this case by subsequent UV–VIS spectra (λ_{max} 369, 475, 533, 606 nm) of the actual sample used for IR spectroscopy. The formulation of the chloro species, $FeCl(TPP)^+$, as an iron(III) complex can be contrasted with the formulation of the oxo species, Fe(O)(TPP)(1-MeIm), as an authentic[19] iron(IV) porphyrin. This illustrates the profound effect that axial ligation can have in dictating the site of redox.[21] A further indication of the utility and generality of this IR criterion for the assignment of $TPP^{+\cdot}$ radical cations is the observation of strong bands near 1280 cm^{-1} in the oxidation products derived from CrCl(TPP) and MnCl(TPP) (see Table I). In view of the formulation of $FeCl(TPP)^+$ as a radical cation it is reasonable to expect $CrCl(TPP)^+$ and $MnCl(TPP)^+$ to be likewise.

Weak bands near 1280 and 1324 cm^{-1} are observed in many octaethylporphyrin (OEP) derivatives, but examination of oxidized

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metal complexes revealed no enhanced intensity in this spectral region. Interestingly, however, a new, strong absorption is noted in the 1520–1570-cm^{-1} region for various oxidized metallooctaethylporphyrins. It should be noted that weaker bands of variable intensity are also seen in this region for oxidized TPP derivatives. A 10-cm^{-1} shift associated with meso deuteration in [Fe(OEP)][ClO$_4$]$_2$ (see Table I) once again serves to indicate assignment to a vibration within the macrocycle. Absence of an enhanced intensity band near 1280 cm^{-1} most likely reflects molecular structural differences rather than electronic configuration differences for OEP vs. TPP compounds. Examination of oxidized [Co(OEP)][X]$_2$ complexes, representation of both the $^2A_{1u}$ and $^2A_{2u}$ radical states,[17] seems to indicate no particular association of radical type with IR spectral type.

In summary, the empirical observation of an IR-active porphyrin ring mode at ~1280 cm^{-1} in TPP$^{+\cdot}$ complexes and at ~1550 cm^{-1} in OEP$^{+\cdot}$ complexes offers an apparently unique criterion for formulating the electronic structures of oxidized metalloporphyrins. The seemingly unambiguous choice between *either* metal-centered *or* porphyrin-centered oxidation in highly oxidized metalloporphyrin complexes can be rationalized by their orbital symmetries. Neither the a_{1u} nor a_{2u} porphyrin HOMO's have the correct symmetry to overlap with any of the metal d orbitals, and this excludes resonance formulations which might lead to ambiguous averaged valencies. Understanding the nature of the highest occupied orbital is probably important for explaining the diverse reactivity patterns of oxidized metalloporphyrins toward nucleophiles or the sites of electron transfer.[9,17] The ~1550-cm^{-1} band of OEP$^{+\cdot}$ complexes may be usefully diagnostic of radical cations in oxidized hemoproteins.[22]

Acknowledgment. Support from NSF grants, CHE 79-10305 (H.M.G.) and CHE 80-26812 (C.A.R.), and NIH grant, GM 28831-01 (H.M.G.), is gratefully acknowledged.

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Carbon-13 Cross-Polarization Magic-Angle-Spinning NMR Study of *n*-Butylamine Adsorbed on γ-Alumina: Characterization of Surface Acid Sites

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The question of surface acidity of aluminum oxides, silicates, and mixed alumina silicates is one of long-standing interest.[1] The problem is one of both practical and theoretical concern. Many industrially important catalytic reactions are based on these materials and, their reactivity is determined to a large extent by the nature of surface acid sites.[1,2] It is of prime interest to identify these catalytically active sites to ascertain whether they are of Brönsted or Lewis type and to determine their relative acidity.

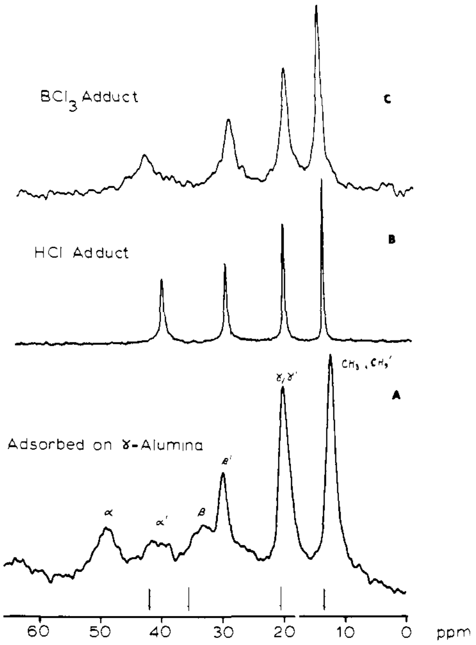

Figure 1. Carbon-13 CP–MAS spectra of *n*-butylamine.[9–11] (a) Adsorbed to the surface of γ-alumina (38 000 accumulations). The vertical bars indicate carbon chemical shifts for liquid-phase *n*-butylamine given in ref 12b; (b) Solid HCl adduct (46 accumulations); (c) solid BCl$_3$ adduct (212 accumulations).

Several methods have been used to study surface acidity, including the most straightforward approach of direct titration with acid–base indicators.[3] Infrared spectroscopy has been extensively employed to examine those interactions involving surface hydroxyl groups.[4] Widespread use of the IR method stems from its sensitivity and adaptability to a variety of adsorbate–adsorbent systems. Proton NMR spectroscopy has similarly provided valuable information that is both quantitative and sensitive to the motions of the adsorbed species.[5] More recently, ^{13}C NMR spectroscopy has been used to advantage.[6,7] For example, Gay and co-workers have employed ^{13}C NMR spectroscopy as a means of following the titration of surface acid sites with aromatic nitrogen bases.[6] To date, such studies have employed standard high-resolution NMR techniques which are able to yield spectra with suitable resolution only in cases where the molecules are undergoing rapid motion on the surface. For the case of strongly adsorbed species, it has been necessary to study the samples at elevated temperatures in order to induce enough motion to sharpen the resonances. This approach represents a serious limitation to investigating the nature of surface–adsorbate interactions by NMR spectroscopy. The recently developed technique of magic–angle spinning in conjunction with dipolar decoupling[8] provides an alternative method of narrowing the lines and avoids this limitation. We report here our cross-polarization magic-angle spinning (CP–MAS) results for *n*-butylamine adsorbed on γ-alumina.[9]

The spectrum of *n*-butylamine on γ-alumina is shown in the Figure 1a.[10,11] There are six prominent resonances, two of which

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[9] The carbon-13 CP–MAS experiments were conducted at 50.3 MHz by using a modified Bruker WP200-WB spectrometer. The single-contact pulse sequence used 50-kHz matching, a contact time (unoptimized) of 1 ms, and a recycle time of 1 s.

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