employing the positions of the second Ge–F stretching mode observed here (axial stretch), and again nearly linear behavior is observed, as shown in Figure 4.

Earlier workers[6] suggested the GeF_4 would form more strongly bound complexes with electron donors than SiF_4, as a consequence of the larger, more diffuse d orbitals on Ge as compared to those on Si, and consequently reduced $p\pi$–$d\pi$ bonding. While the present study does not provide a mechanism for the quantitative determination of ΔH values, some comparisons can be made. The degree of perturbation of the coordinated base qualitatively should measure the strength of interaction. For dimethyl ether complexes of SiF_4 and GeF_4, the symmetric C–O–C stretching mode shifted only 7 cm^{-1} in the SiF_4 complex, compared to 33 cm^{-1} for the GeF_4 complex. For comparison, in the quite strongly bound complex $BBr_3{\cdot}O(CH_3)_2$ a shift of 40 cm^{-1} was observed.[22] This, alone, suggests a substantially stronger interaction with GeF_4 than SiF_4. A second comparison can be made with the methanol complexes of each acid; for the SiF_4 complex no vibrational modes of the perturbed base were observed. This was rationalized in terms of a strength of interaction in $SiF_4{\cdot}CH_3OH$ that was comparable to that of $(CH_3OH)_2$, which is also known to be present. For the $GeF_4{\cdot}CH_3OH$ complex, the perturbed C–O and O–H stretching modes were both observed and showed shifts substantially greater than dimeric methanol. Finally, no perturbed carbonyl stretching mode was noted for the acetone complex[23] of SiF_4, while a shift of more than 40 cm^{-1} was noted for the $GeF_4{\cdot}(CH_3)_2CO$ complex. All of these data, together, indicate that GeF_4 does form substantially stronger complexes with a variety of electron donors than does SiF_4.

As noted above, the spectra do not allow a definitive determination of the structure of the complex, as was obtained for the $GeF_4{\cdot}NH_3$ complex. Nonetheless, the similarity of the spectra of the complexes reported here to that of the $GeF_4{\cdot}NH_3$ complex suggests a structure that is quite similar, particularly for acetone and the better electron donors. In any event, the sharpness of the vibrational modes of the perturbed bases suggests a well-defined specific interaction; one would anticipate similar sharpness for the Ge–F stretching modes were it not for the broadening due to the five naturally abundant germanium isotopes. Finally, the spectra and results presented here add to the rapidly growing body of knowledge concerning molecular complexes and perhaps will stimulate further experimental and theoretical work in this field.

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Resonance Raman Spectra of High Oxidation State Iron Porphyrin Dimers

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Resonance Raman spectra are reported and discussed for a series of single-atom-bridged iron porphyrin dimers, including $(FeTPP)_2C$ and $[(FeTPP)_2N]ClO_4$ (where TPP = 5,10,15,20-tetraphenylporphyrinato), with the use of B-band excitation (4067 Å). The symmetric Fe–X–Fe stretching frequency has been identified by using ^{54}Fe substitution. This band is at 440 and 465 cm^{-1}, respectively, for $(FeTPP)_2C$ and $[(FeTPP)_2N]ClO_4$ in methylene chloride. The Fe–X stretching force constants are estimated to be 4.62 and 5.42 mdyn/Å, respectively, with a stretch–stretch interaction constant of 1.75 mdyn/Å. The large size of these constants indicates substantial π bonding between the iron and the bridging carbon or nitrogen atoms. Using Badger's rule, we estimate that the Fe–N bond length in $(FeTPP)_2N^+$ is 0.05 Å shorter than that for Fe–C in $(FeTPP)_2C$. The core-size marker bands for these two complexes (1564 and 1568 cm^{-1}, respectively) indicate an expansion of 0.015 Å for the former, reflecting the increased nonbonding interaction caused by the shortened bond distances. The porphyrin C–N breathing mode increases for $(FeTPP)_2N^+$ compared to $(FeTPP)_2C$ (1370 vs. 1365 cm^{-1}); this may reflect increased π donation from the bridging carbon to the iron atom. Coordination of pyridine lowers the frequencies associated with the Fe–X–Fe stretch to 424 and 445 cm^{-1}, respectively, and decreases the Fe–X force constants. Pyridine coordination also lowers the core-size marker frequencies (by 8 and 2 cm^{-1} for $(FeTPP)_2$ and $[(FeTPP)_2N]ClO_4$, respectively), presumably as a result of nonbonding interactions between the pyridine and the porphyrin. The C–N breathing frequency of the porphyrin is also lowered (4 and 3 cm^{-1}, respectively), as expected from the decreased effective charge on the iron atom. Changes also occur in the resonant enhancement patterns and are discussed in terms of the electronic structure of these complexes.

Introduction

Iron porphyrin dimers bridged by oxygen, nitrogen, or carbon atoms have attracted recent attention from both experimental[1-8] and theoretical[9] perspectives. The common structural motif shared by these complexes is nearly parallel porphyrin rings connected by a nearly linear Fe–X–Fe bridge. The electron count is easily varied, however, which allows one to observe the effect of electronic structure on a variety of

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physical properties. The currently available catalog of such complexes includes $(FeTPP)_2O$, the isoelectronic pair $(FeTPP)_2O^+$ and $(FeTPP)_2N$, and the isoelectronic triplet of $(FeTPP)_2O^{2+}$, $(FeTPP)_2N^+$, and $(FeTPP)_2C$, where TPP is the 5,10,15,20-tetraphenylporphyrinato(2−) ligand. The μ-oxo dimer[2] is a high-spin Fe(III) species, with strong antiferromagnetic coupling. Oxidation to the mono- or dication gives porphyrin radical complexes of Fe(III).[7,8] With μ-nitrido or μ-carbido dimers, however, the highest lying occupied molecular orbital is primarily metal and bridge atom based. In the μ-nitrido dimer, for example, the unpaired electron is predominantly localized on the iron atoms, as judged by the EPR hyperfine interactions.[10,11] Oxidation to the monocation[5] gives a diamagnetic complex, isoelectronic with the μ-carbido dimer. An analysis of the Mössbauer spectra for these systems indicates[8] increasing charge at the iron atom in the order $(FeTPP)_2N << (FeTPP)_2C < (FeTPP)_2N^+$.

Resonance Raman (RR) spectroscopy has been useful in establishing not only the spin state of the complexes but also information about the nature of the bonding between the iron and the bridging atom. In this paper, the resonance Raman spectra of several of these dimers have been examined, with specific attention to the highly oxidized dimers $(FeTPP)_2C$ and $(FeTPP)_2N^+$. The symmetric Fe–X–Fe stretching vibrations have been previously assigned for $(FeTPP)_2O$[12] and $(FeTPP)_2N$.[13] An assignment of this band for $(FeTPP)_2C$ and $(FeTPP)_2N^+$ is given in this paper.[14a] The force constants, which are calculated from this assignment in conjunction with the infrared-active asymmetric stretch, establish that the Fe–X bond strengths increase in the order $O < N < C < N^+$. The high-frequency RR spectra show porphyrin core size expansion as these bond strengths increase, suggestive of stronger bridging atom–porphyrin nonbonding interactions. Coordination of pyridine to $(FeTPP)_2C$ and $(FeTPP)_2N^+$ yields additional core expansion. Further discussion of variations in the bonding in these systems will be given.

Experimental Section

Compound Preparation. $[(FeTPP)_2N]ClO_4$ and $(FeTPP)_2C$ were prepared as described previously.[8] $^{54}Fe_2O_3$ (purchased from Oak Ridge National Laboratory; 97.08% enriched) was digested in hot concentrated hydrochloric acid to produce $^{54}FeCl_3{\cdot}6H_2O$. The excess acid was removed under vacuum, and the residue was used to metalate H_2TPP.[15] The ^{54}Fe-enriched dimers were prepared in the same manner as the natural-abundance analogues. Compound integrity was monitored with infrared and UV-visible spectroscopies.

Raman spectra were run on dilute (~1 mM) solutions in methylene chloride or pyridine by using 4067-Å excitation from a Spectra Physics 171 Kr^+ laser and a spectrometer consisting of a Spex 1401 double monochromator with a cooled RCA 31034 photomultiplier and photon-counting electronics. Spectra were collected with a Digital MINC computer.

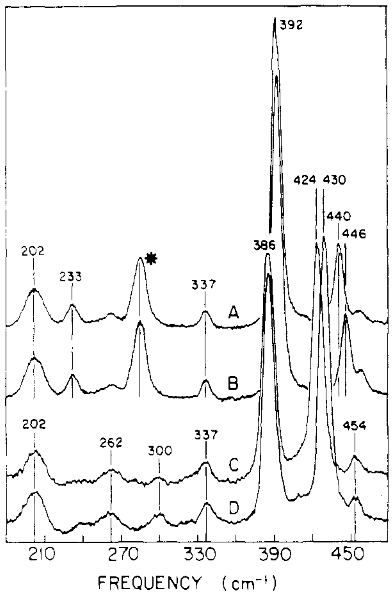

Figure 1. Low-frequency Raman spectra, with 4067-Å excitation, in methylene chloride (A and B) and in pyridine (C and D), of $(FeTPP)_2C$ (A and C) and $(^{54}FeTPP)_2C$ (B and D). Solvent bands are marked by asterisks.

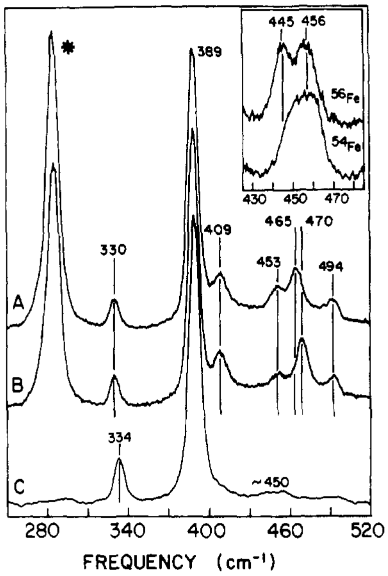

Figure 2. Low-frequency Raman spectra, with 4067-Å excitation, in methylene chloride (A and B) and in pyridine (C and inset), of $[(FeTPP)_2N]ClO_4$ (A and C) and of $[(^{54}FeTPP)_2N]ClO_4$ (B and inset). The inset is a magnification of the 450-cm^{-1} region, showing the ^{54}Fe upshift of the 445-cm^{-1} band. Solvent bands are marked by asterisks.

Results

A. Low-Frequency Vibrations. Figure 1 shows low-frequency RR spectra of $(FeTPP)_2C$ in methylene chloride and in pyridine with 4067-Å excitation. For both solutions, the natural-abundance species is compared with the ^{54}Fe isotopomer. The 6-cm^{-1} increases in frequency, upon ^{54}Fe substitution, of the bands at 440 and 424 cm^{-1} in methylene chloride and pyridine, respectively, identify these bands with the symmetric Fe–X–Fe mode. The theoretical shift for an isolated linear Fe–C–Fe oscillator is 8 cm^{-1}; 5–6-cm^{-1} shifts have also been observed for this mode in the μ-oxo[12] and the μ-nitrido[13] dimers. The 20% difference between observed and expected shifts probably reflects some mixing with porphyrin modes. Figure 2 shows similar spectra for $(FeTPP)_2N^+$. The 5-cm^{-1} increase in frequency upon ^{54}Fe substitution identifies the 465-cm^{-1} band in methylene chloride with $\nu_{Fe-N-Fe}$. The

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Table I. Frequencies (ν_1, cm^{-1}), Force Constants (k, mdyn/Å), and Bond Distances (d, Å) for the Fe-X-Fe Unit in $(FeTPP)_2X$ Species

	X			
	O	N	C	N$^+$
$\nu_{s(Fe-X-Fe)}$	363^a	424^b	440^c	465^c
$\nu_{as(Fe-X-Fe)}$	885^d	918^e	946^f	(1000)^c
k_{Fe-X}^{g}	3.80	4.50	4.62	(5.42)^h
$k_{Fe-X,Fe-X}$	0.16	1.40	1.75	(1.75)^h
d_{Fe-X}	1.763(1)^i	1.661(1)^j	1.675^k	
Δd(X-C)^l	0.088	−0.014		
Δd(X-C)$_{calcd}$^{m}	0.06	0.01		−0.05

^{a} Reference 12. ^{b} Reference 13. ^{c} This work. ^{d} Reference 29. ^{e} Reference 3a. ^{f} Reference 6. ^{g} Calculated for a linear Fe-X-Fe oscillator; k_{Fe-X} is the principal (valence) force constant, $k_{Fe-X,Fe-X}$ is the stretch-stretch interaction constant. ^{h} In this case $k_{Fe-X,Fe-X}$ was assumed to be 1.75 mdyn/Å, and k_{Fe-X} and ν_{as} were calculated. ν_{as} is unassigned but is likely to be at 1003 cm^{-1} (see text). ^{i} Reference 30. ^{j} Reference 3b. ^{k} Reference 31. ^{l} Change in Fe-X bond distance, relative to X = C. ^{m} Change in bond distance as calculated from k_{Fe-X} via Badger's rule:[18] $\Delta d = (a_{ij} - d_{ij})\Delta k^{-1/3}$. For bonds between third- (Fe) and first-row atoms; $a_{ij} = 2.35$ and $d_{ij} = 0.85$, when k is in mdyn/Å.

intensity in this region is greatly diminished in pyridine, but the amplified spectrum in the inset shows that upon ^{54}Fe substitution a weak doublet at 445 and 546 cm^{-1} collapses to a broad single band via an increase in frequency of the 445-cm^{-1} component, which is therefore identified with $\nu_{Fe-N-Fe}$ in pyridine. The remaining bands are porphyrin vibrations. The strong ~390-cm^{-1} band and the weak ~200-cm^{-1} band (not seen for $(FeTPP)_2N^+$) have been assigned[16] to the two lowest frequency A_{1g} modes of the TPP skeleton, ν_8 and ν_9. A slight shift in ν_8 is seen on pyridine binding for $(FeTPP)_2C$ but not for $(FeTPP)_2N^+$. The remaining weak bands probably arise from porphyrin out-of-plane modes;[13] the 453- and 494-cm^{-1} bands are in the frequency region expected for pyrrole folding modes.[17]

The asymmetric Fe–C–Fe stretching mode of $(FeTPP)_2C$ has also been identified in the infrared spectrum at 946 cm^{-1}.[6,14] This permits a calculation of the Fe–C stretching and stretch–stretch interaction force constants for an isolated Fe–C–Fe linear oscillator. The results are shown in Table I and compared with previous calculations for $(FeTPP)_2N$ and $(FeTPP)_2O$. For $(FeTPP)_2N^+$, the location of the asymmetric stretch is uncertain. We examined the infrared spectrum of the perchlorate salt in Nujol mull and in methylene chloride solution but found no obvious candidate band. There was, however, a marked intensification of the 1003-cm^{-1} component of a 1003, 994 cm^{-1} doublet, which is seen in all of the dimer species and probably arises from skeletal or phenyl vibrations. A calculation for the Fe–N–Fe$^+$ oscillator, carried out on the assumption that the stretch–stretch interaction constant is the same as for the Fe–C–Fe oscillator, gave a principal Fe–N force constant of 5.42 mdyn/Å and a predicted asymmetric stretching frequency of 1000 cm^{-1}. Thus it is plausible that the asymmetric stretch does indeed coincide accidentally with the 1003-cm^{-1} component of the porphyrin infrared doublet. (The calculated ^{54}Fe shift for this mode is only 2 cm^{-1}, too small to have been detected in our infrared spectra.)

Also included in Table I are Fe–X bond distances for $(FeTPP)_2X$, with X = O, N, and C, and bond distance differences calculated from the force constants by using Badger's rule.[18] The calculted bond lengthening of $(FeTPP)_2O$ compared to the distance in $(FeTPP)_2C$ is 0.06 Å, in reasonable agreement with the crystallographically determined difference, 0.088 Å. The calculated lengthening for $(FeTPP)_2N$ is 0.01 Å, whereas the crystal structure actually shows a 0.014-Å shortening compared to the distance in $(FeTPP)_2C$; with such small differences, however, the discrepancy is probably not significant. For $(FeTPP)_2N^+$ the bond length is calculated from the estimated force constant to be 0.05 Å shorter than in $(FeTPP)_2C$.

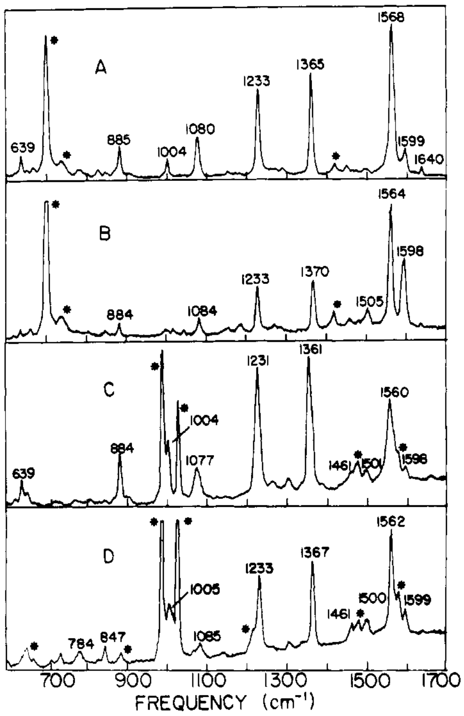

Figure 3. High-frequency Raman spectra, with 4067-Å excitation of (A) $(FeTPP)_2C$ in methylene chloride, (B) $(FeTPP)_2N^+$ in methylene chloride, (C) $(FeTPP)_2C$ in pyridine, and (D) $(FeTPP)_2N^+$ in pyridine. Solvent bands are marked by asterisks.

Pyridine is known to bind to $(FeTPP)_2C$[6] and $(FeTPP)_2N^+$[5] but *not* $(FeTPP)_2N$.[11b] The observed decrease in the symmetric Fe–X–Fe stretching frequency in pyridine might in principle be due either to Fe–X bond weakening or to kinematic changes (i.e. increased Fe effective mass) brought about the additional bonds to pyridine. To investigate this question, we carried out model calculations on a linear pentaatomic oscillator, py–Fe–X–Fe–py, with point mass pyridine ligands. These showed that pyridine binding necessarily *increased* the Fe–X–Fe symmetric stretching frequency (because of interaction with the lower frequency py–Fe mode), unless unreasonably high py–Fe,Fe–X interaction force constants were assumed. Consequently, the observed lowering of $\nu_{Fe-X-Fe}$ implies a weakening of the Fe–X bonds. When a 0.5 mdyn/Å py–Fe force constant was used (with a zero py–Fe,Fe–X interaction constant), the Fe–X force constant, or the Fe–X,-Fe–X interaction constant, or both, had to be lowered by about 1.0 mdyn/Å to accommodate the $\nu_{Fe-X-Fe}$ lowering on pyridine binding. This decrease is close to that found for the Fe–NO bond of NO–heme in NO–hemoglobin upon coordination of the proximal imidazole.[19] A trans effect of similar magnitude is implied. The 0.5 mdyn/Å py–Fe force constant used in this calculation is about half the size of the py–Fe force constant in $(py)_2Fe^{II}$ mesoporphyrin,[20] for which $\nu_{py-Fe-py}$ has been identified at 179 cm^{-1}. We were unable to detect any candidate RR band for the expected py–Fe stretching mode down

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Table II. Polarized RR Band Frequencies (cm^{-1}) for $(FeTPP)_2X$ Species

	$(FeTPP)_2C$ in				$(FeTPP)_2N^+$ in		
assgnt[a]	C_6H_5N[b]	CH_2Cl_2[b]	$CHCl_3$[c]	NaCl/ Na_2WO_4 pellet[d]	CH_2Cl_2[b]	C_6H_5N[b]	$(FeTPP)_2N$ in CS_2[e]
A	1598	1599	1599	1602	1598	1599	1599
ν_2	1560	1568	1569	1571	1560	1562	1567
ν_3	1461						
ν_4	1361	1365	1365	1370	1370	1367	1367
C	1233	1233	1234	1237	1231	1233	1235
ν_5	1084	1080	1081	1085	1077	1085	1080
ν_6	1004	1004		1008		1005	1004
ν_7	884	885			884		
G	639	639	635				
γ_{pyr}					494		
γ_{pyr}	454	454			453	456	
$\nu_{Fe-X-Fe}$	424	440		443	465	445	424
ν_8	396	392	392	394	389	389	386
γ_{por}	337	337	334	338	330	334	336
γ_{por}	262	262		274			267
γ_{por}		233		234			226
ν_9	202	202	204				194

[a] See ref 16. Definitions: A, C, and G, phenyl modes; ν_2-ν_9, A_{1g} skeletal modes of the porphyrin ring; γ_{pyr}, pyrrole folding mode; γ_{por}, porphyrin out-of-plane deformation; $\nu_{Fe-X-Fe}$, symmetric bridge stretch. [b] This work. [c] Reference 26. [d] Reference 14. [e] Reference 13.

to 100 cm^{-1}, the frequency predicted by our calculation. The intensity of this mode appears to be too low to detect.

B. High-Frequency Modes. Figure 3 shows RR spectra from 600 to 1700 cm^{-1} for $(FeTPP)_2C$ and $(FeTPP)_2N^+$ in methylene chloride and pyridine. This region contains porphyrin skeletal modes and vibrations of the phenyl substituents. All of the observed skeletal modes correspond to totally symmetric (A_{1g}) vibrations, as expected for B-band excitation.[21] The frequencies are tabulated in Table II. Of particular interest are the strong bands near 1370 and 1565 cm^{-1}, which are believed to involve mainly stretching of the C–N bonds and outer ring bonds, respectively.[16]

The ~1565-cm^{-1} band has been found by Stong et al.[22] to correlate with the porphyrin core size, C_t–N (the porphyrin center pyrrole nitrogen distance in angstroms), according to the equation

$$\bar{\nu} = 262.5[7.95 - (C_t\text{–N})]$$

The frequency calculated for $(FeTPP)_2C$ from the crystallographic C_t–N distance, 1.963 Å, is 1571 cm^{-1}, in good agreement with the observed value of 1568 cm^{-1}. The slight decrease in this frequency for $(FeTPP)_2N^+$, to 1564 cm^{-1}, implies a 0.015-Å expansion of the porphyrin ring, which is a plausible consequence of the increased nonbonded interactions between the pyrrole nitrogen atoms and the bridging atom associated with the shorter Fe–X bond. In pyridine, the decrease in this frequency for $(FeTPP)_2C$ (to 1560 cm^{-1}) implies a 0.03-Å porphyrin expansion. This presumably reflects the new nonbonded forces produced by the pyridine binding. The decrease is only 2 cm^{-1} for $(FeTPP)_2N^+$, perhaps because the porphyring is already more expanded in this complex.

The ~1370-cm^{-1} C–N stretch is sensitive to both the spin and the oxidation state of the central Fe ion,[23] and it is known in physiological-type porphyrins (with C_b substituents) to be sensitive to the competition between the axial ligands and the porphyrin ring for back-bonding of the d_π electrons.[24] Good π-acceptor ligands increase the frequency,[24] while π-donor ligands, such as thiolate, decrease the frequency.[25] The lowering observed for $(FeTPP)_2C$ relative to $(FeTPP)_2N^+$ (5 cm^{-1}) and even $(FeTPP)_2N$ (2 cm^{-1}) is most readily explained on the basis of stronger π donation[9] from C than from N with attendant increased back-donation to the porphyrin ring. The binding of pyridine decreases this frequency slightly for both $(FeTPP)_2C$ and $(FeTPP)_2N^+$. This is probably because the coordinated pyridine reduces the effective nuclear charge of the iron, thereby increasing the extent of back-donation.

We note that Hofmann and Bocian[14b] found a C–N stretching frequency of 1370 cm^{-1} for $(FeTPP)_2C$ in a $NaCl/Na_2WO_4$ pellet and challenged the earlier report of a 1365-cm^{-1} frequency by Chottard et al.,[26] suggesting that their spectrum had been contaminated by photodecomposition products. However, our spectrum taken in methylene chloride agrees quite well with the reported chloroform solution frequencies of Chottard et al.[26] There is a systematic 3–5-cm^{-1} lowering of all of the frequencies in the high-frequency region relative to the pellet spectrum of Hofmann and Bocian.[14] It is not uncommon to observe systematic shifts of this magnitude between solution and solid-state spectra, and we attribute the discrepancy to this source.

Discussion

Tatsumi and Hoffmann[9] have reported molecular orbital calculations for the Fe–X–Fe bridging system of porphyrin dimers. Substantial interaction is found between the p_x, p_y orbitals of the bridging X atom and the d_π orbitals of the Fe atoms. π donation is expected to be much greater for X = C than for X = N, because the p orbitals are more extended. This is consistent with $(FeTPP)_2C$ having a lower frequency for the ν_4 C–N stretching fundamental than either $(FeTPP)_2N^+$ or $(FeTPP)_2N$. Also consistent with greater π bonding for X = C is the substantial RR intensity seen for the Fe–C–Fe stretching mode (Figure 1) in either methylene chloride or pyridine. For $(FeTPP)_2N$, Schick and Bocian[13] found the Fe–N–Fe stretching mode to be enhanced via a charge-transfer band at 390 nm on the blue side of the B band;

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the charge-transfer absorption was greatly diminished in pyridine solution as was the RR intensity of the Fe–N–Fe band. Likewise for (FeTPP)$_2$N$^+$, we find broad absorption in the B-band region, suggesting a contribution from a charge-transfer transition. The B band narrows considerably in pyridine, suggesting that the charge-transfer band has shifted out of the region; as in the case of (FeTPP)$_2$N, the RR intensity of the Fe–N–Fe band markedly decreases (Figure 2). In the case of (FeTPP)$_2$C, however, the B band is narrow in methylene chloride, while pyridine produces a high-energy shoulder on this band. The Fe–C–Fe band intensity increases substantially in pyridine (Figure 1), suggesting additional enhancement via a new charge-transfer transition. In the absence of such a transition, however, the RR enhancement is much greater for (FeTPP)$_2$C (in methylene chloride) than for (FeTPP)$_2$N$^+$ or (FeTPP)$_2$N (in pyridine). This intrinsic enhancement is attributable to direct coupling to the porphyring π–π^* transition, made effective by the large extent of C–Fe π bonding. Stretching of the C–Fe bond modulates the Fe–porphyrin π interaction and provides a coupling mechanism. The situation is analogous to that found in oxyhemoglobin, for which the high frequency of the Fe–O$_2$ stretch[27] gives evidence for substantial π bonding. The excitation profile for the Fe–O$_2$ stretch shows no evidence for charge-transfer enhancement but simply follows the porphyrin absorption spectrum. This is consistent with direct coupling to the porphyrin π–π^* transition.[28]

For (FeTPP)$_2$C and (FeTPP)$_2$N$^+$, the highest filled orbital is an e$_g$ nonbonding orbital made up of the Fe d$_\pi$ orbitals.[9] (FeTPP)$_2$N, however, has an extra electron that is predicted to go into an a$_{1g}$ antibonding oribtal with mainly d$_{z^2}$ character.[9] Analysis of the EPR spectrum of (FeTPP)$_2$N confirms that the unpaired electron resides in an a$_{1g}$ orbital with mostly Fe charcter.[11a] Curiously, however, the Fe–X bond distance is nearly the same for (FeTPP)$_2$C as for (FeTPP)$_2$N, despite the antibonding electron of the latter. It may be that the electron is largely localized on the side of the Fe atoms away from the bridge (presumably by mixing in of iron 4p$_z$ orbital character). Consistent with this is the absence of pyridine adduct formation[11b] in the case of (FeTPP)$_2$N. When the latter is dissolved in pyridine, the excited state is influenced, as evidenced by the diminution of the charge-transfer band intensity,[13] but there is no perturbation of the ground state. The Fe–N–Fe stretching band, although much weaker, is unshifted in frequency. In contrast, both (FeTPP)$_2$C and (FeTPP)$_2$N$^+$ do form well-defined adducts,[5,6] and the lowering in frequency of the Fe–X–Fe stretch reflects appreciable weakening of the Fe–X bonds, as discussed above.

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Registry No. (FeTPP)$_2$C, 75249-87-5; (^{54}FeTPP)$_2$C, 92669-36-8; [(FeTPP)$_2$N]ClO$_4$, 83967-78-6; [(^{54}FeTPP)$_2$N]ClO$_4$, 92669-38-0; (FeTPP)$_2$N$^+$, 78591-88-5.

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Solvent Effects in the Complexation of Dibenzo-14-crown-4 and Its Analogues with Lithium Ion

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The lithium-7 NMR spectroscopic results for the complexation of lithium ion with the crown ether dibenzo-14-crown-4 (DB14C4) and its methyl (Me-DB14C4), *tert*-butyl (*t*-Bu-DB14C4), and di-*tert*-butyl (*t*-Bu$_2$-DB14C4) derivatives in acetonitrile (ACN), propylene carbonate (PC), acetone (AC), tetrahydrofuran (THF), pyridine (py), dimethyl sulfoxide (Me$_2$SO), and dimethylformamide (DMF) are discussed. In solvents of medium or low donor number the 1:1 complex was formed, and there was no clear-cut evidence for the existence of 2:1 complexes. The formation of complexes is strongly influenced by the solvent, and the stability of these complexes varies inversely with the donor number of solvents. Different substituent groups on the benzene ring of the crown ethers can also influence the stability of the complexes, and the stability sequence is Me-DB14C4 > *t*-Bu-DB14C4 > *t*-Bu$_2$-DB14C4 > DB14C4. The substituent effect on the reaction has also been found to be quite significant along with the solvent effect.

Introduction

Since Pedersen first synthesized macrocyclic polyethers[1] (crown ethers) as very effective complexing agents for the alkali-metal and alkaline-earth-metal cations,[2] there has been considerable interest shown in the chemical and physical properties of these compounds. There are many parameters[2,3] that determine the stability and the selectivity of crown ether complexation with metal ions, such as cavity size of the ligand, cation diameter, spatial distribution of ring binding sites, the character of the heteroatoms, the presence of additional binding sites, and the type of solvent. Although it is already known that the substituent effect is very significant for por-

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