heats of adsorption. It has already been shown that heats of adsorption have similar values to heats of reactions in the gas phase.[37,38] Two qualitative similarities can be noted between our work and surface phenomena. If a species has too high a heat of chemisorption, it will be too tenaciously held to the surface and will retard its catalytic activity. Common catalytic poisons are nitrogen and phosphorus donors. Reactions of olefins are commonly catalyzed by metal surfaces. The relative displacement energies of the nitrogen and phosphorus donors are much higher than the polyolefins consistent with these observations. In studies involving competitive adsorption, apparently diolefins are chemisorbed more strongly than simple olefins.[36] We have found that the displacement energy of two monoolefins is less than all the polyolefins studied here.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and to the National Defense Educational Act, Grant No. 70.02605.1, for a fellowship to E. F. H.

(37) D. O. Hayward and B. M. W. Trapnell, "Chemisorption," Butterworths, London, 1964, p 208.

(38) J. M. Thomas and W. J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis," Academic Press, New York, N. Y., 1967, p 314.

Synthesis and Far-Infrared Spectra of Ferric Octaethylporphine Complexes

H. Ogoshi, E. Watanabe, Z. Yoshida, J. Kincaid, and K. Nakamoto*

Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan, and the Todd Wehr Chemistry Building, Marquette University, Milwaukee, Wisconsin 53233. *Received November 7, 1972*

Abstract: Ferric octaethylporphine (OEP) complexes of the types Fe(OEP)X ($X^- = CH_3COO^-, F^-, Cl^-, Br^-, I^-, N_3^-$, and NCS^-) and $[Fe(OEP)L_2](ClO_4)$ (L = γ-picoline, imidazole and benzimidazole) have been prepared, and their infrared spectra have been measured in the 4000–100-cm^{-1} region. The Fe–N(OEP), Fe–X, and Fe–L stretching bands have been assigned based on metal isotope substitution (^{54}Fe/^{56}Fe).

Heme coenzymes are of great importance in biological systems and as such have been investigated extensively by chemists. In hemoglobin, the iron is in the ferrous state, whereas it is in the ferric state in cytochromes and methemoglobin.

Ferric porphyrins containing axial ligands have been studied by a number of physicochemical methods. X-Ray analyses have been carried out on methoxyiron(III) mesoporphyrin IX dimethyl ester,[1] chloroiron(III) tetraphenylporphine[2] and bis(imidazole)tetraphenylporphinatoiron(III) chloride.[3] Mössbauer spectroscopy has been used extensively to study the structure and bonding of these and related complexes.[4–6] Proton magnetic resonance spectra have been reported,[7,8] and electronic spectra have been measured and assigned.[9,10] According to these investigations, ferric complexes containing axial ligands can be high or low spin depending upon the temperature and the nature of the axial ligand. In general, the central metal–nitrogen skeleton is square pyramidal in high-spin complexes and square planar in low-spin complexes.

Thus far, almost no infrared studies have been reported in ferric porphyrin complexes containing axial ligands. It is anticipated that low-frequency infrared spectra will provide valuable information about the structure of the complex and the strength of the iron–ligand bonds. The main purposes of this paper are to report the facile preparation of ferric octaethylporphine (OEP) complexes containing axial ligands and to correlate their far-infrared spectra with structural and bonding information obtained by other methods.

Experimental Section

Preparation of Compounds. Octaethylporphine (OEP) was prepared according to the method of Inhoffen, *et al.*,[11] and purified by chromatography on alumina (Brockmann Grade III) with chloroform.[12] Deep red crystals were obtained by recrystallization from a chloroform–methanol mixture.

Fe(OEP)(CH$_3$COO). Finely pulverized iron metal (120 mg) was refluxed in 30 ml of glacial acetic acid under nitrogen until iron powder was dissolved.[11] After 100 mg of OEP was added to this solution, it was maintained under gentle refluxing for 1 hr and allowed to cool to room temperature. Air was introduced into the reaction mixture for several hours. Lustrous blue-black crystals were collected, washed with ether, and dried in air. Recrystallization from acetic acid yielded 100 mg of Fe(OEP)(CH$_3$OO).

Fe(OEP)X ($X^- = F^-, Cl^-, Br^-, I^-, N_3^-$, and NCS^-). A chloro-

---

(1) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Amer. Chem. Soc.*, **87**, 2312 (1965).

(2) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Amer. Chem. Soc.*, **89**, 1992 (1967).

(3) D. M. Collins, R. Countryman, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 2066 (1972); **91**, 5166 (1969).

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

(5) P. L. Richard, W. S. Caughey, H. Eberspaecher, G. Feher, and M. Malley, *J. Chem. Phys.*, 47, 1187 (1967).

(6) T. H. Moss, A. J. Bearden, and W. S. Caughey, *J. Chem. Phys.*, **51**, 2624 (1969).

(7) W. S. Caughey and L. F. Johnson, *Chem. Commun.*, 1362 (1969).

(8) H. A. O. Hill and K. G. Morallee, *J. Amer. Chem. Soc.*, **94**, 731 (1972).

(9) W. A. Eaton, *J. Chem. Phys.*, **49**, 985 (1968).

(10) M. Zenner, M. Gouterman, and H. Kobayashi, *Theor. Chim. Acta*, **8**, 26 (1967).

(11) H. H. Inhoffen, J. H. Fuhrhop, H. Voigt, and H. Brockmann, Jr., *Justus Liebigs Ann. Chem.*, **695**, 133 (1966).

(12) R. Countryman, D. M. Collins, and J. L. Hoard, *J. Amer. Chem. Soc.*, **91**, 5166 (1969).

Table I. Results of Microanalysis

Compound	Formula	% C Found	% C Calcd	% H Found	% H Calcd	% N Found	% N Calcd
Fe(OEP)(CH_3COO)	$C_{38}H_{47}N_4O_2Fe$	70.05	70.47	7.21	7.32	8.52	8.65
Fe(OEP)F	$C_{36}H_{44}N_4FFe$	70.22	71.16	7.11	7.30	8.78	9.22
Fe(OEP)Cl	$C_{36}H_{44}N_4ClFe$	69.53	69.25	7.21	7.09	8.81	8.92
Fe(OEP)Br	$C_{36}H_{44}N_4BrFe$	65.35	64.66	6.78	6.63	7.92	8.38
Fe(OPE)I	$C_{36}H_{44}N_4IFe$	60.21	60.43	6.21	6.20	7.53	7.82
Fe(OEP)N_3	$C_{36}H_{44}N_7Fe$	67.97	68.56	7.05	7.03	15.27	15.55
Fe(OEP)NCS	$C_{37}H_{44}SFe$	67.79	68.72	6.84	6.86	10.62	10.83
[Fe(OEP)(γ-pic)$_2$]ClO_4	$C_{48}H_{58}N_6ClO_4Fe$	66.13	65.93	6.80	6.68	9.52	9.61
[Fe(OEP)(imid)$_2$]ClO_4	$C_{42}H_{52}N_8ClO_4Fe$	61.26	61.20	6.48	6.36	13.30	13.60
[Fe(OEP)(bimid)$_2$]ClO_4	$C_{50}H_{56}N_8ClO_4Fe$	64.28	64.97	6.22	6.11	12.09	12.12

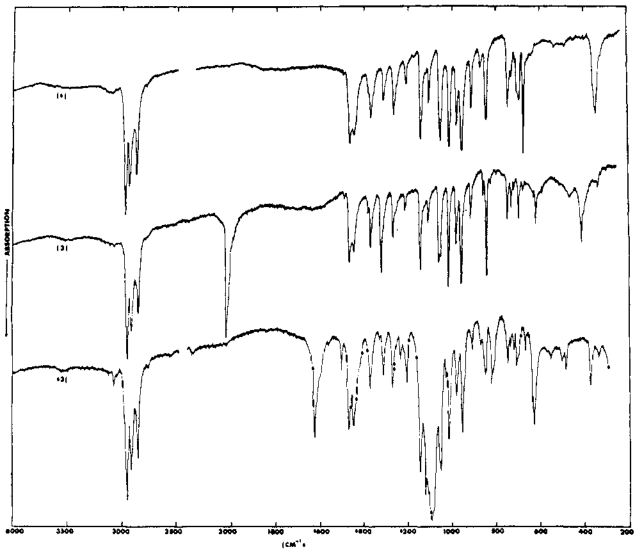

Figure 1. Infrared spectra of (1) Fe(OEP)Cl, (2) Fe(OEP)N_3, and (3) [Fe(OEP)(γ-pic)$_2$]ClO_4 in the high-frequency region.

form solution of Fe(OEP)(CH_3COO) was added to a saturated aqueous solution of sodium salt of the respective anion. The reaction mixture was vigorously stirred until the acetate complex was converted to Fe(OEP)X. Progress of the reaction was monitored by measuring the visible spectrum of the solution. After the chloroform layer was separated from the water layer. the former was washed with several portions of water, dried over anhydrous sodium sulfate, and evaporated to dryness on steam bath under reduced pressure. The resulting solid was recrystallized from dry benzene. An alternative method to prepare Fe(OEP)Cl has been reported by Whitlock, *et al.*[13]

[Fe(OEP)(γ-picoline)$_2$]ClO_4. To 120 mg of Fe(OEP)Cl in 50 ml of benzene was added 100 mg of $AgClO_4$. The reaction mixture was gently refluxed for 20 min. Freshly distilled γ-picoline (1.5 ml) was added dropwise to the reaction mixture which was further refluxed for 45 min. The mixture was cooled to room temperature and filtered. The solid material thus obtained was washed with water several times and dried over P_2O_5 under vacuum. The dried solid was continuously extracted with chloroform. After removal of chloroform, recrystallization from petroleum ether–chloroform gave 70 mg of fine dark red crystals. Infrared peaks due to γ-picoline appear at 1625, 1609, 1509, 819. 509, and 489 cm^{-1}.

[Fe(OEP)(imidazole)$_2$]ClO_4. To 600 mg of Fe(OEP)Cl dissolved in 200 ml of benzene was added 800 mg of $AgClO_4$, and the reaction mixture was refluxed for 3 hr. After adding 300 mg of imidazole dissolved in 50 ml of benzene, the reaction mixture was refluxed continuously until the color of the solution became transparent. The precipitate was separated by filtration, and the product was extracted with chloroform. [Fe(OEP)(imidazole)$_2$]ClO_4 was obtained by removing chloroform under reduced pressure. Recrystallization from chloroform–benzene (3:1 mixture) yielded 450 mg of dark brown crystals. Infrared peaks due to imidazole are observed at 3240, 1505, 1329, and 658 cm^{-1}.

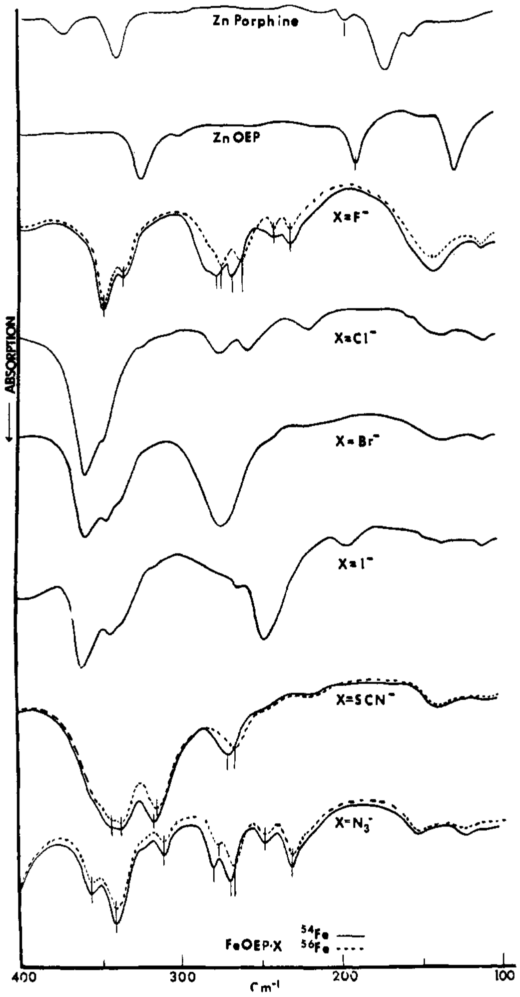

Figure 2. Far-infrared spectra of zinc porphine, ZnOEP, and Fe(OEP)X. For X = F, NCS, and N_3, the solid line indicates the spectrum of the ^{54}Fe complex whereas the dotted line shows the spectrum of the corresponding ^{56}Fe complex.

[Fe(OEP)(benzimidazole)$_2$]ClO_4. To 120 mg of Fe(OEP)Cl dissolved in 150 ml of xylene was added 140 mg of $AgClO_4$. The procedure which follows is similar to that described above for the imidazole complex. Recrystallization from chloroform gave 84 mg of dark violet crystals. Infrared peaks due to benzimidazole are observed at 3150, 1624, 1598, 1418, 1300, 771, 762, 545, 432, and 419 cm^{-1}.

The presence of the N–H stretching band near 3200 cm^{-1} in the above two compounds indicates that these amines coordinate to the Fe atom through the aza nitrogen (—N=).

Metal Complexes Containing ^{54}Fe and ^{56}Fe. Iron isotopes were received from Oak Ridge National Laboratory in the form of

---

(13) H. W. Whitlock, Jr., R. Hanauer, M. Y. Oester, and B. K. Bower, *J. Amer. Chem. Soc.*, 91, 7486 (1969).

Fe_2O_3. The purity of the isotopes was ^{54}Fe, 96.81%, and ^{56}Fe, 99.93%. Ferric oxide was reduced to metallic iron by passing hydrogen gas over it at 400° for 4 hr. ^{56}Fe (53.5 mg) was refluxed in 50 ml of glacial acetic acid for 1 hr and 350 mg of OEP was added to this solution. ^{56}Fe(OEP)(CH_3COO) thus obtained was used to prepare other isotopic complexes. The corresponding ^{54}Fe complexes were prepared by the same procedure. The purity of these isotopic compounds was checked by comparing their infrared spectra with those containing iron of natural abundance for which microanalysis was performed as shown in Table I.

Spectral Measurements. Infrared spectra were measured on a Beckman IR-12(4000-250 cm^{-1}) and a Hitachi Perkin-Elmer FIS-3(410-33 cm^{-1}) infrared spectrophotometer. The KBr pellet technique was used for the 4000-300-cm^{-1} region, and the Nujol mull technique with polyethylene plates was used for the 410-100-cm^{-1} region. To observe small shifts due to metal isotope substitution, the spectra were run on an expanded scale with a scanning speed of 2 cm^{-1}/min. Reproducibility of the spectra was checked by multiple scans over the desired frequency range. Calibration of the frequency reading was made by recording the spectra of polystyrene, indene, and water vapor. Figure 1 illustrates the infrared spectra of the chloro, azido, and γ-picoline complexes in the high-frequency region. As expected, the spectra of these and other complexes studied here are very similar to those of other OEP complexes[14] in this region.

Results and Discussion

Fe(OEP)X (X = F, Cl, Br, I, N_3, and NCS). Figure 2 illustrates the far-infrared spectra of the Fe(OEP)X series together with those of zinc porphine and ZnOEP, and Table II lists the observed frequencies and band assignments. Each complex exhibits at least five bands (A, B, C, D, and E) in addition to the Fe–X stretching band. These five bands have been assigned based on the results of normal coordinate analysis on zinc porphine[15] and the ^{54}Fe–^{56}Fe isotope experiment. For zinc porphine, the following assignments have been made previously.

Table II. Far-Infrared Frequencies, Metal Isotope Shifts, and Band Assignments of the Fe(OEP)X Type Complexes (cm^{-1})

	Fe–X str	A	B	C	D	E
Zinc porphine	...	381	349	206	182	167
ZnOEP	...	334	310	203	150	121
Fe(OEP)F[c]	605.5 (3)	346	334	277 (3) 266 (3)	241 231	143
Fe(OEP)Cl	357[a]	357[a]	347	275 256	220	140
Fe(OEP)Br	270[a]	355	344	270[a] ...[b]	225	140
Fe(OEP)I	246	357	340	263 ...[b]	196	...
Fe(OEP)NCS[c]	315 (1.5)	354	343 336	270 (4)	219	140
Fe(OEP)N_3[c]	421 (3)	355	340 310	280 (3) 270 (2.5)	248 232	155 125

[a] Overlapped band. [b] Hidden band. [c] Frequencies of the ^{54}Fe complex. Numbers in parentheses indicate the metal isotope shift, $\tilde{\nu}(^{54}Fe)-\tilde{\nu}(^{56}Fe)$.

band A	(381 cm^{-1})	porphine core in-plane bend
band B	(349 cm^{-1})	porphine core in-plane bend
band C	(206 cm^{-1})	Zn–N stretch coupled with porphine core bend
band D	(182 cm^{-1})	skeletal out-of-plane bend
band E	(167 cm^{-1})	

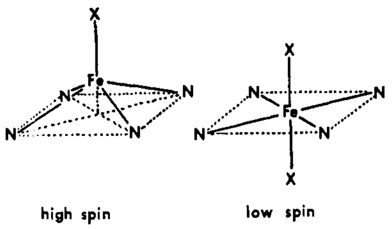

Figure 3. Structures of square-pyramidal and square-planar FeN_4 skeletons.

Among these bands, only C is metal isotope sensitive. Thus, band C can be assigned easily by examining the metal isotope shift. Bands A and B are not metal isotope sensitive. Furthermore, their frequencies do not change appreciably by changing the metal. Bands D and E are not metal isotope sensitive since they are bending modes. However, they are shifted appreciably by changing the metal. The axial Fe–X stretching band is also metal isotope sensitive. However, this band can be distinguished easily from band C since the former is shifted markedly by changing the ligand X. Based on these criteria, band assignments shown in Table II have been established.

In the case of Fe(OEP)F, the bands at 605.5, 277, and 266 cm^{-1} are shifted by *ca.* 3 cm^{-1} while all other bands are not shifted by the ^{54}Fe–^{56}Fe substitution. The band at 605.5 cm^{-1} is definitely due to the Fe–F stretching since it is metal isotope sensitive and other halogeno complexes do not exhibit this band. Then, the latter two must be assigned to band C which is predominantly due to the Fe–N stretching mode.

The spectra of the chloro, bromo, and iodo complexes are similar to that of the fluoro complex except for the overlapping of the Fe–X stretching with other low-frequency metalloporphyrin bands (see Table II). The CN stretching band at 2042 cm^{-1} (strong) and the NCS bending band at 480 cm^{-1} (weak) indicate the presence of Fe–N(CS) bonding in Fe(OEP)NCS.[16] The CS stretching band could not be identified because of the complexity of the spectrum in the 850–700-cm^{-1} region. Fe(OEP)N_3 exhibits four bands at 2060, 1327, 629, and 421 cm^{-1} which are reasonably assigned to the asymmetric and symmetric N_3 stretching, N_3 bending, and Fe–N_3 stretching modes, respectively. Only the last band is metal isotope sensitive. Below 400 cm^{-1}, it exhibits two isotope sensitive bands at 280 and 270 cm^{-1} (band C).

According to X-ray analysis, the Fe atom of Fe(TPP)Cl is in a square-pyramidal environment and is displaced by 0.5 Å from the basal plane of the four nitrogen atoms toward the chlorine atom.[2] A similar deviation of the Fe atom is seen in methoxyiron(III) mesoporphyrin IX dimethyl ester (0.46 Å).[1] The symmetry of such square-pyramidal skeletons is C_{4v} as is shown in Figure 3. Under C_{4v} symmetry, two Fe–N(OEP) stretching modes are expected to be infrared active (A_1 and E). The fact that two Fe–N(OEP) stretching modes (band C) are observed for most of the compounds studied here suggests that the FeN_4 skeletons of these complexes are square pyramidal and the Fe atoms are off the basal plane by an appreciable distance. The only exception is the NCS complex which exhibits one Fe–N(OEP) stretching mode.

---

(14) H. Ogoshi, N. Masai, Z. Yoshida, J. Takemoto, and K. Nakamoto, *Bull. Chem. Soc. Jap.*, **44**, 49 (1971).

(15) H. Ogoshi, Y. Saito, and K. Nakamoto, *J. Chem. Phys.*, **57**, 4194 (1972).

(16) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).

Table III. Far-Infrared Frequencies, Metal Isotope Shifts, and Band Assignments of the $[Fe(OEP)L_2]^+$ Type Ions (cm^{-1})[a]

	Fe–L str	A	B	C	D	E
$[Fe(OEP)(\gamma\text{-pic})_2]ClO_4$[b]	373 (2.5)	341 (0.5)	341 (0.5)	303 (2.5)	229	
$[Fe(OEP)(imid)_2]ClO_4$[b]	376.5 (3.5)	355 (3)	340 (1)	319 (1)	244	166
$[Fe(OEP)(bimid)_2]ClO_4$	333[c]	344	333[c]	294	236	179

[a] All these complexes exhibit ClO_4 bands at 1100–1080 and 620 cm^{-1}. In addition, the following bands have been assigned to amines: 226 cm^{-1} (pyridine), 271 and 251 (benzimidazole). [b] Frequencies of the ^{54}Fe complex. Numbers in parentheses indicate the metal isotope shift, $\bar{\nu}(^{54}Fe)-\bar{\nu}(^{56}Fe)$. [c] Overlapped band.

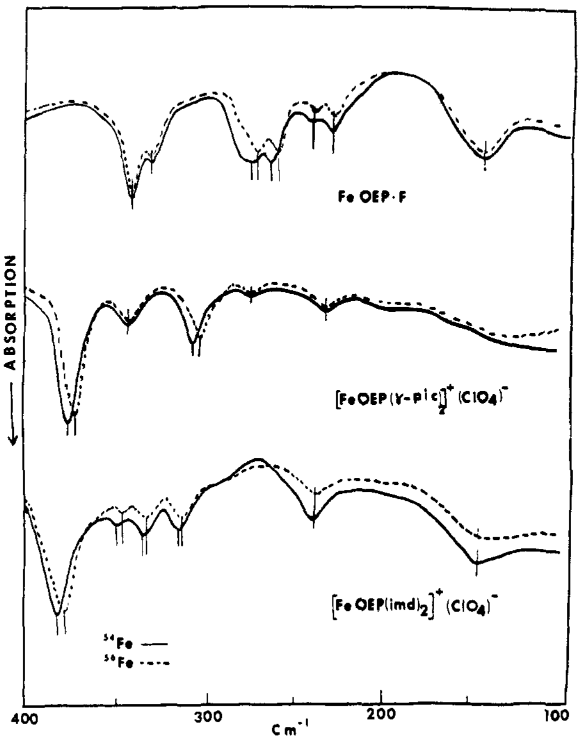

Figure 4. Far-infrared spectra of Fe(OEP)F, $[Fe(OEP)(\gamma\text{-pic})_2]ClO_4$, and $[Fe(OEP)(imid)_2]ClO_4$. The solid line indicates the spectrum of the ^{54}Fe complex whereas the dotted line indicates the spectrum of the ^{56}Fe complex.

This may indicate that the deviation of the Fe atom from the basal plane is small so that two bands are too closely located to be observed as separate bands. The electronic spectra of all these complexes indicate that the Fe atoms are in the high-spin configuration.[9,17]

It should also be noted that the Fe–N(OEP) stretching frequencies of these Fe(III) complexes (280–250 cm^{-1}) are relatively high compared with OEP complexes of other metals[14]

Zn(II) <	Mg(II) <	Cu(II) <	Co(II) <	Ni(II)
203	214	234	265	287 cm^{-1}

The metal–nitrogen stretching frequency is governed by several factors such as oxidation state of the metal, coordination number, and the possibility of π bonding, etc. In the present case, the effect of increasing the coordination number which tends to decrease the frequency is offset by that of increasing the oxidation number which tends to increase the frequency.[18]

$[Fe(OEP)L_2]ClO_4$ (L = γ-Picoline, Imidazole, and Benzimidazole). Although many bis-amine adducts of ferric porphyrins are known in solution,[8] thus far only one compound, $[Fe(TPP)(imidazole)_2]Cl\cdot(CH_3OH)_2$, has been isolated.[4] In this work, we have isolated $[Fe(OEP)L_2]ClO_4$ where L is γ-picoline, imidazole, and benzimidazole.

Figure 4 illustrates the far-infrared spectra and Table III gives the observed frequencies and band assignments of these compounds. The γ-picoline complex exhibits two bands at 373 and 303 cm^{-1} which are metal isotope sensitive. The former is assigned to the Fe–γ-pic stretching band because it does not appear in the Fe(OEP)X series discussed previously. The latter must be assigned to the Fe–N(OEP) stretching mode (bond C) since it is the only other band which is isotope sensitive. The slight shift of the 341-cm^{-1} band is on the borderline of our experimental error. However, a slight shift may arise due to vibrational coupling as is pointed out in the discussion of the spectra of the bis-imidazole complex.

The imidazole complex exhibits a strong band at 376.5 cm^{-1} which does not appear in the simpler complexes. This band is shifted by 3.5 cm^{-1} on the ^{54}Fe–^{56}Fe substitution. Thus, it is most reasonable to assign it to the Fe–N (imidazole) stretching mode. This frequency is very close to the axial Fe–N stretching frequency (381 cm^{-1}) of bis(L-histidine methyl ester)-protohemin.[19] Although the band at 355.5 cm^{-1} (very weak) also gives a relatively large isotope shift (3.0 cm^{-1}), it has been assigned to vibration A. This large isotopic shift has been attributed to the vibrational coupling between vibration A and vibration C. Such vibrational coupling has been observed for Ni(OEP).[15,20] Vibration B (340 cm^{-1}) is also metal isotope sensitive as a result of such vibrational coupling. Since all other bands below 300 cm^{-1} are not metal isotope sensitive, we have assigned the 319-cm^{-1} band to vibration C.

The far-infrared spectrum of the bis-benzimidazole complex is similar to that of the imidazole complex; it exhibits a strong band at 333 cm^{-1} which is interpreted as an overlap of the Fe–N(benzimidazole) stretching and vibration B. Vibration C is assigned at 294 cm^{-1}. The Fe–N(benzimidazole) stretching frequency (333 cm^{-1}) is much lower than the Fe–N-(imidazole) stretching frequency (376.5 cm^{-1}) because of two reasons: (1) the mass of the former ligand is larger than that of the latter, and (2) the Fe–N bond of the former is weaker than that of the latter because of steric effect of the bulky benzimidazole group.

It should be noted that only one Fe–N(OEP) stretching band is assignable in all these complexes. This result is in agreement with X-ray analysis which

---

(17) Z. Yoshida, E. Watanabe, and H. Ogoshi, to be submitted for publication.

(18) R. J. H. Clark, *Spectrochim. Acta*, 21, 955 (1965).

(19) A. van der Heijden, H. G. Peer, and A. H. A. van den Oord, *Chem. Commun.*, 369 (1971).

(20) H. Bürger, K. Burczyk, and J. H. Fuhrhop, *Tetrahedron*, 27, 3257 (1971).

shows that the Fe atom in [Fe(TPP)(imidazole)$_2$]Cl is on the N_4 basal plane.[3] The electronic spectra of Fe(OEP)L$_2$ (L = imidazole and benzimidazole) show that both compounds are of low spin.[17] In fact, the magnetic moment of the imidazole complex was found to be 2.03 BM at room temperature.[17] Mössbauer data also indicate that the bis-imidazole complex is of low spin.[4] On the other hand, all the Fe(OEP)X type complexes are of high spin.[6,7,21]

In going from high- to low-spin complexes, electrons are shifted from the iron e_g* to t_{2g} orbitals. The iron atom in low-spin ferric porphyrin complexes is known to be a π-electron donor,[22] and its t_{2g} orbitals may overlap with vacant π-orbitals of the porphyrin ring to form π bonds.[23] Ligands such as imidazole are relatively good π donors in these complexes, reenforcing back-donation to the vacant porphyrin π orbitals.[24] This increase in π bonding may account for higher Fe–N(OEP) stretching frequencies of bis complexes relative to those of monocomplexes.[25]

Acknowledgments. H. O., E. W., and Z. Y. acknowledge the support from Nishina Foundation. J. K. was supported by an NDEA fellowship. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

---

[21] C. Maricondi, W. Swift, and D. K. Straub, *J. Amer. Chem. Soc.*, **91**, 5205 (1969).

[22] P. S. Braterman, R. C. Davies, and R. J. P. Williams, *Advan. Chem. Phys.*, 3, 394 (1964).

[23] J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, Amsterdam, 1964, p 55.

[24] L. M. Epstein, D. K. Straub, and C. Maricondi, *Inorg. Chem.*, **6**, 1723 (1967).

[25] Y. Saito, J. Takemoto, B. Hutchinson, and K. Nakamoto, *Inorg. Chem.*, **11**, 2003 (1972).

Thermochemistry, Calculations, and the Barrier to Ring Closure in Short-Chain-Length Diradicals[1]

L. M. Stephenson,* T. A. Gibson, and J. I. Brauman

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. Received October 30, 1972

Abstract: A comparison of thermochemical and quantum chemical analyses of the energetics of short-chain-length diradicals is made. It is concluded that either all present quantum calculations inadequately treat diradical interactions or that 1,3 and 1,4 diradicals suffer a previously unrecognized destabilizing effect relative to a classical model.

Thermochemical and quantum chemical analyses of the properties of 1,3 and 1,4 diradicals have generated widely disparate points of view. The thermochemical analysis, due initially to Benson and coworkers,[2] depicts these diradicals as *intermediates* with substantial (6–10 kcal/mol) barriers associated with the ring-closure reaction, while numerous quantum calculations[3–6] show potential energy surfaces without minima in the region of bond-broken small ring compounds. In this paper we comment on the origin of this discrepancy and point out implications for diradicals associated with a combination of these two treatments.

Thermochemical Calculations

In recent years, the accumulation of a substantial body of experimentally based thermodynamic data for simple organic compounds and radicals has made the thermochemical approach to mechanistic problems an extremely attractive one. Using simple group and bond additivity relationships, Benson and coworkers[7] have accurately estimated heats and entropies of formation for a variety of species. A number of applications of this method have been summarized,[7] and it now appears that the practice of comparing calculated and experimental heats and entropies will join other more classical methods such as the use of stereochemistry as a primary tool in mechanistic work. However, it should be kept in mind that the thermochemical method is a formalism useful in evaluating the energy of *models* of chemical species. While well-chosen models often lead to energy evaluations closely matching experimental data, such matching cannot in general be interpreted *a priori* as evidence for the accuracy of the model in representing the details of the actual chemical entity under consideration.

Apparent exceptions to the wide applicability of the thermochemical method occur in analyses of cyclopropane and cyclobutane ring-opening reactions. Typical results (Scheme I) for the pyrolysis of cyclobutane and cyclopropane derivatives make clear the appeal which bond-broken species have in understanding the courses of these reactions. Benson and O'Neal[2] attempted to analyze these reactions in terms of *hypothetical* noninteracting 1,3 and 1,4 diradical intermediates and have calculated the heats of formation of such

---

[1] The Chemistry of Diradicals. IV. For part III, see L. M. Stephenson and T. A. Gibson, *J. Amer. Chem. Soc.*, **94**, 4599 (1972).

[2] *Cf.* E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 72, 1866 (1968), and references contained.

[3] A. K. Q. Siu, W. M. St. John, III, and E. F. Hayes, *J. Amer. Chem. Soc.*, 92, 7249 (1970).

[4] J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *ibid.*, **94**, 279 (1972).

[5] (a) R. Hoffmann, *ibid.*, 90, 1475 (1968); (b) R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *ibid.*, **92**, 7091 (1970).

[6] P. J. Hay, W. J. Hunt, and W. A. Goddard, III, *ibid.*, **94**, 638 (1972).

[7] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, and references contained.