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Resonance Raman Spectra of Iron(II) Cytochrome P_{450} Model Complexes: Influence of the Thiolate Ligand[1a]

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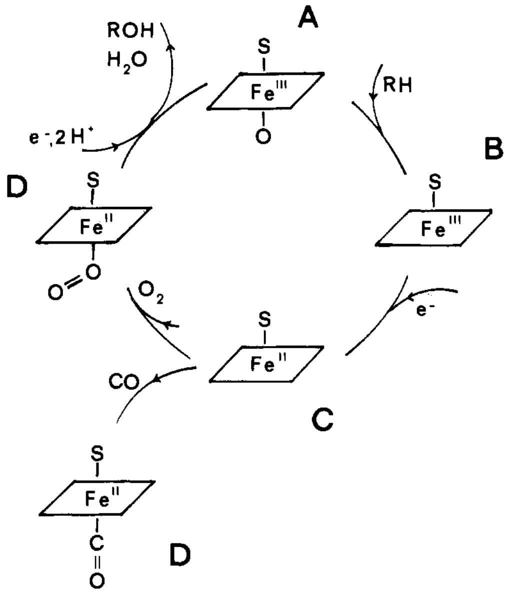
Resonance Raman spectra of model complexes for reduced cytochrome P_{450} and its carbonyl and dioxygen adducts have been obtained with Soret excitation. The frequencies of the main porphyrin vibrations do not stress any specific influence of the thiolate ligand. Isotopic substitution permits assignment of the 479-cm^{-1} Raman line of Fe(TpivPP)($C_6HF_4S^-$)(CO) to the Fe–CO stretching vibration and the 1140-cm^{-1} Raman line of Fe(TpivPP)($C_6HF_4S^-$)(O_2) to the O–O stretching vibration. These frequencies are discussed with special reference to the CO and O_2 adducts of Fe(TpivPP)(*N*-MeIm), a model complex for Mb and Hb. The concomitant weakening of the Fe–CO and CO vibrational frequencies of Fe(TpivPP)($C_6HF_4S^-$)(CO) is explained by the σ-donor character of the thiolate ligand.

Cytochrome P_{450} is a membrane-bound hemoprotein that catalyzes the hydroxylation and epoxidation of a large variety of hydrophobic molecules. It belongs to a monoxygenase enzymatic system that is an essential part of the detoxification process. The catalytic cycle of cytochrome P_{450} includes four stable and isolable states: a low-spin ferric resting state A, a substrate-bound high-spin ferric state B, a high-spin ferrous state C, and a low-spin ferrous dioxygen state D (Scheme I). When the system in state C is exposed to carbon monoxide instead of oxygen, a low-spin ferrous carbonyl state D′ is generated. For more insight into the structure and bonding around the iron atom, model compounds based on a thiolate-bound iron porphyrin have been prepared and their spectroscopic properties compared to those of the actual enzymatic states.[1b-d] X-ray structural data have been obtained for a B Fe(III) state model[2] and more recently for C, D, and D′ Fe(II) state models.[3,4]

Resonance Raman (RR) spectroscopy is a very sensitive technique for the specific investigation of the active site of hemoproteins. RR spectra have been obtained for cytochrome P_{450} from various origins.[5-7] In reduced state C, they all show an unusually low frequency for the so-called "oxidation state marker" band.[8a] For the Fe(III) states the "spin marker" frequencies[8a] were used to monitor the spin equilibrium. The RR spectrum of the pentacoordinated Fe(III) complex Fe(PPIXDME)(SC_6H_4-*p*-NO_2)[8b] has been investigated and probed as a model for state B.[9] Recently, the Fe–S stretching mode has been detected at 351 cm^{-1} in Fe(III) substrate-bound cytochrome P_{450} from *Pseudomonas putida*.[10]

In this paper we describe the RR spectra of the Fe(II) complex Fe(TpivPP)($C_6HF_4S^-$) and its dioxygen and carbonyl adducts, models for states C, D, and D′ of the cytochrome P_{450} catalytic cycle. The influence of the thiolate ligand on the porphyrin bonding is ascertained by comparing (i) different Fe(II) porphyrin complexes and (ii) complexes with thiolate ligands of different reducing abilities. This leads to the conclusion that the π-electron-donor character of the thiolate ligand does not induce a significant extra lowering of the porphyrin frequencies and, therefore, is not the main origin of the low frequencies observed for cytochrome P_{450}.[5-7] For the carbonyl adduct the Fe–CO stretching vibration is observed at 479 cm^{-1}, whereas for the dioxygen adduct the O–O stretching vibration is observed at 1140 cm^{-1}. These values are compared to those obtained for complexes with other trans ligands. The variation observed for the Fe–CO and the CO frequencies are rationalized by considering the thiolate ligand as a σ-donor ligand.

Scheme I



Experimental Section

The complex Fe(TpivPP)($C_6HF_4S^-$)Na^+18C6 was prepared in chlorobenzene solution, following the procedure described in ref 11.

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[8] (a) Spiro, T. G.; Burke, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 5482. (b) Abbreviations: PPIXDME, dianion of protoporphyrin IX dimethyl ester; TpivPP, dianion of *meso*-$\alpha,\alpha,\alpha,\alpha$-tetrakis(*o*-(pivalamido)-phenyl)porphyrin; TPP, dianion of tetraphenylporphyrin; *N*-MeIm, *N*-methylimidazole; py, pyridine; THF, tetrahydrofuran; Mb, myoglobin; Hb, hemoglobin; 18C6, 18-crown-6 ether; C_{222}, 222 cryptand.

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Table I. Raman Frequencies (cm^{-1}) of Fe(TpivPP)(L)(L′) Complexes

$C_6HF_4S^-$	$C_6HF_4O^-$	OH^-	Cl^-	$(C_6HF_4S^-)CO$	$(C_6HF_4S^-)O_2$	assgnt
1544	1545		1545	1566	1566	ν_2
				1501	1502	
1490			1492			ν_{19}
1451			1453			
1434	1434	1437	1435			
1354	1354	1355	1355			
1342	1343	1345	1343	1363	1366	ν_4
				1311		
				1299		
1275	1275	1277	1275	1275		
1250	1252	1252	1251	1255	1253	C_m-Ph
			1220			
1202	1203	1205	1203	1205	1208	C_m-Ph
					1140	O–O
1101	1104	1104	1103	1104		
1070	1070		1069		1073	
986	987	986	988	997		$C_\alpha C_m$
888		890		887		
640	640	638	639	639	640	
				615	615	
593			593	597		
				479		Fe–CO
				445		
				427		
370	369	371	369	380	379	
				322		
288			282		298	
205			209			
193						
			155			

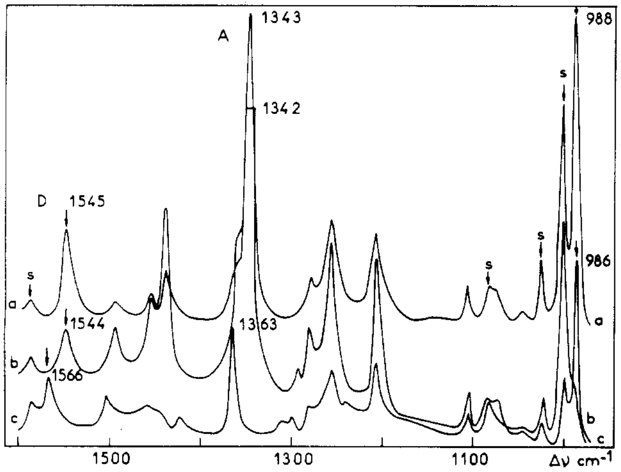

Figure 1. High-frequency RR spectra of iron(II) picket fence porphyrins in C_6H_5Cl solutions (solvent bands indicated by S), at −30 °C: (a) Fe(TpivPP)(Cl^-)Na^+C_{222}, λ_0 = 454.5 nm; (b) Fe(TpivPP)($C_6HF_4S^-$)Na^+18C6, λ_0 = 430 nm; (c) Fe(TpivPP)($C_6HF_4S^-$)(CO)Na^+18C6, λ_0 = 454.5 nm.

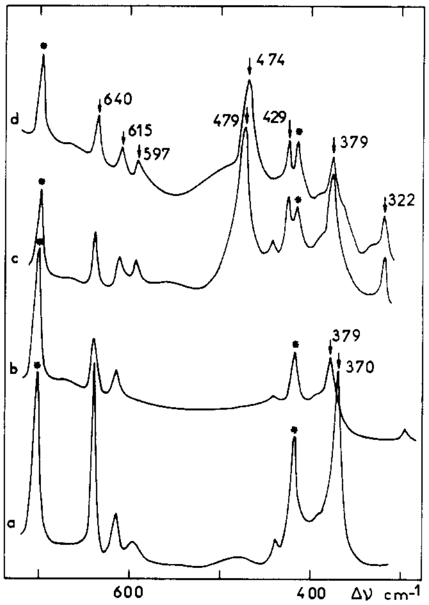

Figure 2. Low-frequency RR spectra of iron(II) picket fence porphyrins in C_6H_5Cl solutions (solvent bands indicated by S), at −30 °C: (a) Fe(TpivPP)($C_6HF_4S^-$)Na^+18C6, λ_0 = 454.5 nm; (b) Fe(TpivPP)($C_6HF_4S^-$)(O_2)Na^+18C6, λ_0 = 440 nm; (c) Fe(TpivPP)($C_6HF_4S^-$)(^{12}CO)Na^+18C6, λ_0 = 454.5 nm; (d) Fe(TpivPP)($C_6HF_4S^-$)(^{13}CO)Na^+18C6, λ_0 = 454.5 nm.

The other pentacoordinated complexes were obtained by reacting cryptated KCl, KOH, or KOC_6HF_4 instead of the thiolate ($C_6HF_4S^-$)Na^+18C6. The dioxygen and carbonyl complexes were generated by bubbling CO or O_2 gas into the thiolate solution. $^{18}O_2$ (98.6% ^{18}O) and ^{13}CO (99% ^{13}C) from the Bureau des Isotopes Stables, CEA-CEN, Saclay, were used to prepare the corresponding isotopically substituted complexes. The pentacoordinated species were examined in fluorescence cells sealed under Ar atmosphere, whereas the CO and O_2 adducts were examined in rotating cells to minimize photodissociation of the sixth ligand. A homemade cryostat allowed the temperature of the solution to be kept at ca. −30 °C during the measurements. UV–visible absorption was used to check the solutions before and after the Raman measurements.

The Raman spectra were recorded on a Coderg double monochromator using a spectral slit width of 5 cm^{-1}; the frequency accuracy was ±1 cm^{-1}. Soret excitation was obtained either from the 454.5-nm line of an Ar^+ laser or from a dye laser using stilbene 3 pumped by the 360-nm lines of a CW Ar^+ laser (laser power at the sample 20 mW).

Results

The Raman spectra of the complexes Fe^{II}(TpivPP)(X^-), with X = C_6HF_4S, $(CH_3)_3CS$, C_6HF_4O, Cl, and OH, and Fe(TpivPP)($C_6HF_4S^-$)(L), with L = CO and O_2 (Figures 1 and 2), were observed with exciting frequencies close to the Soret absorption frequency; in most cases, strong fluorescence of the samples precludes any excitation within the $\alpha\beta$ absorption bands (the chloro derivative was the only one that could be studied with a large range of λ_0). It follows that the Raman bands observed belong to totally symmetric vibrations (the 1354-cm^{-1} band is the only depolarized mode to show

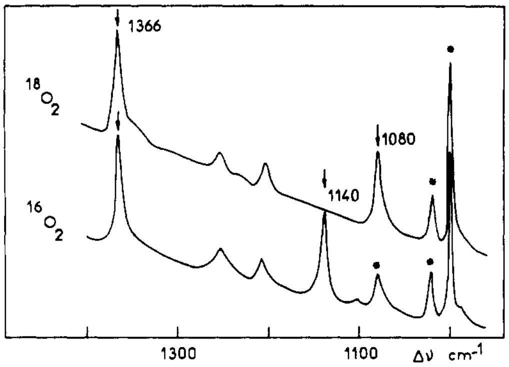

Figure 3. Isotopic effect on the RR spectrum of Fe(TpivPP)($C_6HF_4S^-$)(O_2) (λ_0 = 440 nm): (a) $^{16}O_2$ adduct; (b) $^{18}O_2$ adduct.

noticeable intensity). The Raman frequencies are given in Table I. They mostly correspond to porphyrin modes and, for some of them, to meso-phenyl substituent modes. The assignments are based on Spiro's work.[12]

All the pentacoordinated complexes exhibit very similar spectra so that interference of vibrations belonging to the axial ligand can be discarded. These spectra are also clearly different from that of Fe(TpivPP), ruling out any photoejection of the fifth ligand. With use of a nomenclature derived from a normal-coordinate analysis of octaethylporphyrin vibrations,[13] line ν_4, the so-called "oxidation state marker" line, is located at 1342–1345 cm^{-1}, and line ν_2 is located at 1544–1545 cm^{-1}. Line ν_{19} (spin-state marker) and line ν_{12} (pentacoordination marker) do not show up clearly on the spectra, as they are non totally symmetric. In the case of the chloro derivative, line ν_{19} can be located at 1492 cm^{-1} by using 530.8-nm excitation. (In our previous paper,[14] lines ν_4, ν_2, ν_{19}, and ν_{12} were labeled respectively A, D, C, and B.) With Soret excitation, two other intense lines are observed at 986 and 370 cm^{-1}.

Binding of a sixth ligand induces a general increase of these frequencies, due to the accompanying spin change of the iron atom: a 20-cm^{-1} shift is observed for ν_4 and ν_2 and a 10-cm^{-1} shift for the 370- and 986-cm^{-1} bands. The sensitivity of the latter band was not previously noticed.

The carbonyl derivative Fe(TpivPP)($C_6HF_4S^-$)(CO) exhibits a strong low-frequency mode at 479 cm^{-1} (Figure 2), whose assignment is based on the following experiments:

(i) Under dissociative conditions (static cell) this band disappears and the spectrum of the RS^- complex is obtained; when the CO ligand is allowed to recombine (rotating cell), the band reappears.

(ii) The ^{13}CO adduct shows a Raman spectrum identical with that of the ^{12}CO adduct, but the specific band is located at 474 cm^{-1}. This frequency lowering is in good agreement with a calculated shift of 5 cm^{-1} for the stretching vibration of the Fe–C moiety from the harmonic oscillator approximation.

This leads to the assignment of the 479-cm^{-1} band to the Fe–CO stretching vibration.

Intensity measurements show that maximum enhancement is obtained for this mode close to the maximum of the Soret peak.

The dioxygen derivative exhibits a strong line at 1140 cm^{-1} (Figure 3). This line is specific for the dioxygen complex: it disappears when the O_2 ligand is dissociated and reappears when the O_2 ligand recombines. If $^{18}O_2$ is used to prepare the dioxygen complex, the 1140-cm^{-1} line is no longer present but a new line occurs at 1080 cm^{-1}. A 65-cm^{-1} shift upon $^{18}O_2$ substitution is calculated for the O–O stretching vibration, in the harmonic oscillator approximation, in good agreement with the observed shift. The 1140-cm^{-1} band is therefore assigned to the O–O stretching vibration. No specific line involving the oxygen ligand is detectable in the low-frequency region.

Table II. ν_4 Frequencies (cm^{-1}) of Model Compounds and Corresponding Hemoproteins

		penta-coordinated species	CO adduct	O_2 adduct
model Fe^{II}(TpivPP)	$C_6HF_4S^-$	1342[a]	1363[a]	1366[a]
	$(CH_3)_3CS^-$	1343[a]		
	N-MeIm	1344[b]	1365[c]	1366[b]
hemoprotein	P_{448_1} (PB)[d]	1347[e]	1365[e]	
	P_{448_1} (MC)[d]	1346[e]		
	P_{450} (CAM)[d]	1346[e]	1368[e]	
	P_{450} SCC[d]	1342[e]	1367[e]	
	P_{450_1}[d]	1341[e]		
	Mb	1355[e]	1370[e]	
	Hb	1358[e]	1372[e]	1377[f]

[a] This work. [b] Data for Fe(TpivPP)(2-MeIm).[15] [c] Data for Fe(TPP)(py)(CO).[14] [d] The various cytochromes P_{450} are named after their origin: P_{448_1}, phenobarbital- (PB-) or 3-methylcholanthrene- (MC-) induced rabbit liver microsomes; P_{450} (CAM), camphor- (CAM-) grown *Pseudomonas putida*; P_{450} SCC, adrenal cortex mitochondria; P_{450_1}, phenobarbital-induced rabbit liver microsomes. [e] Reference 7. [f] Reference 8.

Discussion

Porphyrin Vibrations. Very low frequencies of the so-called "oxidation state marker" line have been observed for reduced cytochrome P_{450} (see Table II) and also to a lesser extent for its carbonyl derivative; this has been attributed to the influence of the π-donor character of the thiolate ligand.[5,7]

For the model compounds, we also observed low values for the ν_4 frequency. No direct comparison of the RR frequencies of the model complexes and of the hemoprotein derivatives can be made due to the different substituent pattern present in the porphyrin chromophores. However we expect to find the same trend in frequency shifts upon identical variations of the same parameter (here the nature of the axial ligand) in both series. The large body of data available for FeTPP derivatives[14,15] allows us to discriminate between the influence of the basicity of the thiolate ligand and the influence of other structural and bonding parameters.

Let us consider first the pentacoordinated derivatives. The ν_4 frequency is 1342 cm^{-1} for the $C_6HF_4S^-$ complex but is also 1345 cm^{-1} for the hydroxo complex, 1343 cm^{-1} for the chloro complex, and 1343 cm^{-1} for the alcoholate complex. Therefore, low frequencies are obtained for all the anionic ligand derivatives examined so far. All these complexes are high spin. The only other ν_4 frequency known for a Fe(II) high-spin derivative is that of Fe(TPP)(2-MeIm). Its value, 1345 cm^{-1}, is not very different from those observed for the anionic ligands. Therefore, the low values for the ν_4 frequency reflect mostly the influence of the spin of the iron atom. ν_4 sensitivity to spin effects was previously noticed[14,15] but is more soundly established with the larger set of data presented here. The types of ligands investigated until now do not allow a thorough test of the sensitivity to π effects within the high-spin Fe^{II}TPP series.[29]

For Fe(II) natural hemes, ν_4 sensitivity to spin effects has been also noticed,[14] but there is little evidence for the dependence of ν_4 on π effects in the case of high-spin hemes.

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Table III. Fe–CO (RR Data) and C–O (IR Data except *i*) Stretching Frequencies (cm^{-1}) for Fe(TpivPP)(L)(CO) Model Complexes and Carbonyl Hemoproteins HpCO

	L	ν_{Fe-CO}	ν_{CO}
model complexes	C$_6$HF$_4$S$^-$	479[a]	1956[b]
Fe(TpivPP)(L)(CO)	CH$_3$S$^-$		1945[c]
	(CH$_3$)$_3$CS$^-$		1935[d]
	CH$_3$(CH$_2$)$_3$S$^-$		1923[c]
	py	486[e]	1980[f]
	N-MeIm	489[e]	1969[g]
	THF	526[e]	1955[h]
hemoproteins-CO	P$_{450}$ (CAM)		1940[c]
	Mb	512[i]	1944[i]

[a] This work. [b] Reference 11. [c] Reference 21. [d] Reference 24. [e] Reference 17. [f] Reference 20. [g] Reference 19. [h] Reference 18. [i] Reference 22.

Looking at the hemoprotein data (Table II), one notices an average 10-cm^{-1} decrease of the ν_4 frequency between deoxy Hb or Mb and ferrous cytochrome P$_{450}$. This is not reproduced when one substitutes a thiolate ligand for imidazole in the model compounds. One may argue that an arenethiolate is different from a cysteinate. However our investigation of the 2-methylpropane-2-thiolate derivative does not show any significant difference between the two thiolates (Table II). Therefore, our data suggest that the frequency lowering observed for the hemoproteins is due to the local environment of the heme, at least in part. In keeping with this line of reasoning, a fairly large range of frequencies is observed for cytochromes P$_{450}$ of different origins.

The introduction of a sixth ligand on the model compound leads to the expected increase of ν_4 frequency accompanying the high-spin to low-spin change, and again little or no difference is observed between the thiolate and imidazole derivatives. For example, ν_4 is located at 1366 cm^{-1} for the dioxygen adducts Fe(TpivPP)(C$_6$HF$_4$S$^-$)(O$_2$) and Fe(TpivPP)(*N*-MeIm)(O$_2$),[15] and for the carbonyl derivatives ν_4 is located at 1363 cm^{-1} for Fe(TpivPP)(C$_6$HF$_4$S$^-$)(CO) and at 1365 cm^{-1} for Fe(TPP)(py)(CO).[14] For the hemoproteins the presence of CO partly wipes out the frequency differences observed for Mb or Hb and cytochrome P$_{450}$. In the case of the carbonyl model complex, the minor influence of the RS$^-$ ligand on the porphyrin vibrations is rather unexpected, owing to the known interaction of high-energy filled sulfur orbitals with the e$_g$ π^* orbital of the porphyrin, responsible for the typical splitting of the Soret absorption band.[16]

Fe–CO Vibration. We observed the Fe–CO stretching vibration at 479 cm^{-1} for Fe(TpivPP)(C$_6$HF$_4$S$^-$)(CO). Recently Yu has observed the Fe–CO frequencies of the analogous complexes Fe(TpivPP)(py)(CO), Fe(TpivPP)(*N*-MeIm)(CO), and Fe(TpivPP)(THF)(CO) at 486, 489, and 526 cm^{-1}, respectively.[17] Assuming that all these Fe–CO bonds are linear, he has deduced a frequency sensitivity to bond length changes of 6 cm^{-1}/0.01 Å. The X-ray data show that in Fe(TpivPP)(C$_2$H$_5$S$^-$)(CO) and Fe(TTP)(C$_2$H$_5$S$^-$)(CO) the Fe–CO bond is linear and the Fe–C distances range from 1.78 to 1.81 Å.[3,24] Using the previously mentioned relationship, we would expect a Fe–CO frequency of ca. 485–465 cm^{-1} for the thiolate complexes, in good agreement with the observed frequency. Due to the absence of Fe–CO distortion, the Fe–C stretching frequency can be considered as indicative of bond strength; thus, it appears that the Fe–C bond strength decreases in the order THF > *N*-MeIm > py > C$_6$HF$_4$S$^-$. Considering the corresponding CO stretching frequencies, obtained by IR measurements (Table III), one gets the following order for the CO bond strength: THF $\simeq$ C$_6$HF$_4$S$^-$ < *N*-MeIm < py. Obviously the position of the thiolate anion is at variance in the two series.

Table IV. Fe–O$_2$ and O–O Stretching Frequencies (cm^{-1})

	ν_{Fe-O}	ν_{O-O}
Fe(TpivPP)(C$_6$HF$_4$S$^-$)O$_2$		1140[a]
Fe(TpivPP)(*N*-MeIm)O$_2$	568[b]	1159[c]
HbO$_2$	567[d] or 571[e]	1107 and 1156[f]

[a] RR, this work. [b] RR, ref 15. [c] IR, ref 19. [d] RR, ref 27. [e] RR, ref 26. [f] IR, ref 28.

The classical π-bonding scheme allows one to rationalize the influence of ligand L in the L–Fe–CO moiety when L is THF or a nitrogenous base. THF, having no π-acceptor character, does not compete with CO for the iron dπ electrons, thus allowing an important Fe–CO back-bonding; this leads to an increase of the π^* population on CO and thus to a decrease of the CO frequency and a concomitant increase of the Fe–C frequency. L ligands with increasing π-acceptor abilities compete more and more effeciently for the iron dπ electrons, leading to a decrease of the iron back-bonding toward CO. As a consequence, the Fe–C bond is weakened and the C–O bond is strengthened. This is what is observed for the nitrogenous base. The reverse trend is to be expected for a donor L ligand. But the RS$^-$ ligand does not fit into this scheme, as both the Fe–C and the C–O bonds are weakened. To explain this result, we have to consider the σ interactions. The RS$^-$ anion being a good σ donor induces a decrease of the σ bonding of CO to Fe, evidenced by the decrease of the ν_{Fe-C} frequency. The resulting increase of σ-electron population on CO leads to a decrease of the CO bond strength as the σ orbitals on CO have a slightly antibonding character.[23] Accordingly, one observes even lower CO frequencies for alkanethiolate complexes.[3,21,24] To confirm this analysis, further work is in progress with other anionic ligands of varying π-donor abilities. For the hemoproteins, no significant differences in CO frequencies are observed between P$_{450}$–CO and MbCO.[21] But in this case changes in bonding geometry and hydrogen bonding are expected to perturb the CO frequencies and obscure the trans-ligand influence.

O–O Vibration. The O–O stretching vibration is located at 1140 cm^{-1} in the Raman spectrum of Fe(TpivPP)(C$_6$HF$_4$S$^-$)(O$_2$), but the Fe–O$_2$ stretching mode is not observed in the low-frequency region. The reverse holds for the Raman spectrum of Fe(TpivPP)(*N*-MeIm)(O$_2$): the Fe–O$_2$ vibration is observed at 568 cm^{-1}, and the O–O vibration remains unobserved.[15] However, the latter frequency (1159 cm^{-1}) can be obtained from the IR spectrum.[19] X-ray structural data[4,25] point to the same overall bent end-on geometry of the Fe–O$_2$ moiety in both complexes but with a different major orientation of the O$_2$ entity with respect to the Fe–N$_p$ bonds. This orientational discrepancy may be of no importance when dealing with the complexes in solutions as, in this case, we expect the O$_2$ entity to show more degrees of

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freedom, even at −30 °C. The structural analogy of the two complexes allows one to compare their O–O stretching frequencies. Both are located in the superoxide region. A 19-cm^{-1} decrease is observed for ν_{O-O} when *N*-MeIm is replaced by $C_6HF_4S^-$. This is in agreement with the shift observed for the ν_{C-O} of the carbonyl adducts. This stresses again the influence of the σ-donor properties of the thiolate toward the trans ligand. The different RR activities shown by the Fe–O_2 and the O–O modes are difficult to rationalize in the absence of excitation profiles for these modes. In the case of MbO_2 (or HbO_2), where only the Fe–O_2 vibration is RR active, direct coupling of this mode to the porphyrin π–π* transition is favored.[26] Since the same RR activity was observed for the model complex Fe(TpivPP)(*N*-MeIm)(O_2), the same mechanism may be operative. It is quite possible that the enhancement of the O–O vibration as observed for Fe(TpivPP)($C_6HF_4S^-$)(O_2) originates in a different electronic process.

In conclusion, the RR spectrum of Fe(TpivPP)($C_6HF_4S^-$) is typical of high-spin ferrous complexes. No significant influence of the π-donor properties of the thiolate ligand is observed; however, the sensitivity of RR frequencies to π interactions, in the case of high-spin ferrous complexes, is not well documented. For the carbonyl and oxygen low-spin ferrous complexes, the porphyrin ring, CO, Fe–CO, and O–O vibrations also show a lack of sensitivity to the π-donor properties of the thiolate ligand. The concomitant decrease of the Fe–CO and CO frequencies is explained by the σ-donor character of the thiolate ligand.

Registry No. Fe^{II}(TpivPP)($C_6HF_4S^-$), 86161-44-6; Fe^{II}(TpivPP)($C_6HF_4O^-$), 93403-09-9; Fe^{II}(TpivPP)(OH), 93452-45-0; Fe^{II}(TpivPP)(Cl), 93452-46-1; Fe(TpivPP)($C_6HF_4S^-$)(CO), 86161-84-4; Fe(TpivPP)($C_6HF_4S^-$)(O_2), 86124-04-1; CO, 630-08-0; O_2, 7782-44-7.

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Spectrophotometric Studies of Iodine Complexes in an Aluminum Chloride–Butylpyridinium Chloride Ionic Liquid

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Iodine, iodine chloride, tetraethylammonium iodide, and tetraethylammonium triiodide solutions in aluminum chloride–*N*-1-butylpyridinium chloride ambient-temperature ionic liquids have been studied by UV–visible spectrophotometry. The different oxidation states of iodine show a distinct dependence on the solvent acidity. Iodine(1+) exists in the form of ICl in acidic melts and in the form of ICl_2^- in basic $AlCl_3$–BuPyCl mixtures. Molecular iodine does not form strong complexes in acidic or neutral solutions. Triiodide ion is stable in neutral butylpyridinium tetrachloroaluminate, but not in acidic melts. In solutions of iodine or triiodide in basic $AlCl_3$–BuPyCl ionic liquids equilibrium mixtures of I_2Cl^-, I_3^-, ICl_2^-, and I^- are formed. The charge-transfer bands observed for iodide solutions in neutral and basic melts reveal the formation of iodide ion–butylpyridinium cation ion pairs. Similar bands in pure basic $AlCl_3$–BuPyCl mixtures indicate the association of chloride ion and butylpyridinium cation.

Introduction

Our electrochemical investigations of iodine in aluminum chloride–*N*-1-butylpyridinium chloride (BuPyCl) ambient-temperature molten salts[1,2] showed that in this solvent iodine and its compounds are involved in extensive acid–base and redox equilibria. Variations in the $AlCl_3$:BuPyCl mole ratio lead to wide changes in Lewis acidity of the medium. Neutral equimolar mixture of $AlCl_3$ and BuPyCl can be made acidic by adding excess $AlCl_3$ or basic with excess BuPyCl. The present study was undertaken to obtain additional information on interactions of iodine in different oxidation states with the ionic solvent. The electrochemical experiments did not directly identify all the iodine species formed in basic $AlCl_3$–BuPyCl ionic liquid.[2] They did not indicate the formation of I_2^+ ion in acidic ambient-temperature melts although this ion has been postulated on the basis of spectral results for mixtures of I_2 and Cl_2 dissolved in high-temperature $AlCl_3$–NaCl molten salts.[3]

It was also of interest to seek in this medium, containing a high concentration of butylpyridinium cation, charge-transfer bands for iodide and chloride ions. Charge transfer (CT) transitions for alkylpyridinium iodides have been observed in many different solvents.[4-7] CT bands have also been reported for myristylpyridinium chloride solutions in chloroform.[6] It was assumed[5-7] that these transitions occur for contact ion pairs; a possible contribution of solvent-separated ion pairs to ionic association equilibria in these systems was however unclear.[6-8] Ionic association equilibria in $AlCl_3$–BuPyCl ionic liquids are different in this respect in that in this medium only contact ion pairs should be formed. Formation of this type of ionic association between butylpyridinium cation and iodide and chloride ions is indicated by charge-transfer bands reported herein.

Experimental Section

The procedures used for purification of $AlCl_3$ (Fluka), synthesis and purification of *N*-1-butylpyridinium chloride, and preparation

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