appear to conflict with the data reported here that show that the C-terminal site releases iron more quickly at 72 mM concentrations of ligand. However, the published data on iron removal by PP_i were collected at a lower pH (6.9), which may selectively labilize the N-terminal site. In addition, the earlier studies have been conducted by using 1–3 mM concentrations of PP_i, with EDTA or desferrioxamine as a thermodynamic sink for the released iron. At low concentrations of PP_i, the predominant reaction pathway is the saturation process. The salt effects on the monoferric transferrins reported here were measured at 72 mM ligand, where the predominant reaction pathway is the first-order process (k'''). The apparent inversion of the relative lability of the two sites toward PP_i may be related to the change in the predominant iron removal pathway for high and low concentrations of PP_i. Additional data at low ligand concentration are needed for a phosphonic acid chelating agent with greater iron-binding affinity than PP_i, so that the iron is completely removed even at low ligand concentrations.

The effects of chloride and perchlorate on iron removal from monoferric transferrins are generally consistent with previous studies.[27,28] In all cases studied thus far, perchlorate accelerates iron release from the C-terminal site and retards iron release from the N-terminal site. Chloride also consistently accelerates iron

release from the C-terminal site. However, the effect of chloride on the N-terminal site is not consistent. Baldwin and de Sousa reported that chloride causes only a minor decrease in the rate constant for iron removal from N-terminal monoferric transferrin by EDTA. Chasteen et al. report a sharp decrease in the rate constant for iron removal by 1 mM PP_i from the N-terminal site of diferric transferrin. We observe a significant reduction in the rate constant for iron removal by NTP but only a minor decrease in the rate constant for 72 mM PP_i. It appears that iron release from the N-terminal site is more sensitive to factors such as temperature and the identity and concentration of the competing ligand.

Contribution from the Faculty of Pharmaceutical Sciences, University of Tokushima, Sho-machi 1, Tokushima 770, Japan, Department of Chemistry, Faculty of Science, Ehime University, Matsuyama, Ehime 790, Japan, and Department of Material Science, Technology University of Nagaoka, Kamitomioka, Nagaoka, Ni-igata 949-54, Japan

Unusual Hyperporphyrin Spectra for Bis(thiolato)rhodium(III) Octaethylporphyrins and Generation of the Superoxide Anion by the Complexes

Hiromu Sakurai,*,† Harumi Uchikubo,† Kazuhiko Ishizu,‡ Kunihiko Tajima,‡ Yasuhiro Aoyama,§ and Hisanobu Ogoshi§

Bis(thiolato) complexes of rhodium(III) octaethylporphyrin (Rh^{III}(OEP)) exhibiting a "split Soret band" with peaks at about 370 nm and 450 nm, classified as a "hyperporphyrin spectrum", were prepared with Rh^{III}(OEP)Cl, aliphatic or aromatic thiol compounds, and tetrabutylammonium hydroxide in organic solvents. The structure of the complexes was characterized by comparing their electronic absorption spectra with the spectra of thiolato adducts of cytochrome P-450 and its cobalt-substituted enzymes, bis(thiolato)iron(III)–, cobalt(III)–, and Cr(III)–porphyrin complexes reported previously. These complexes were stable under air at room temperature, their apparent half-lives being over 30 min, monitored by the intensities of the split Soret band. The split Soret band correlated well with the dielectric constants of alcohols as solvents and with the Hammett σ values of the substituents of thiophenol derivatives as axial ligands on Rh^{II}(OEP) in benzene and acetone solvents. Under the same conditions observed for the formation of the hyperporphyrin spectra, the generation of the free superoxide anion was detectable by ESR spectrometry at 77 K. On the basis of the results, the possible reaction mechanism generating the superoxide anion by a bis(thiolato)–Rh^{III}(OEP) complex was proposed.

Introduction

Cytochrome P-450 enzymes (P-450) catalyze the incorporation of one of the two atoms of molecular oxygen into a wide variety of organic compounds.[1] In activation of molecular oxygen, P-450 is unusual and unique in that the axial fifth ligand trans to the molecular oxygen binding to iron(III) protoporphyrin IX (protoheme) has been revealed to be a negatively charged cysteinato sulfur, on the basis of recent X-ray structure analysis.[2] P-450 in the reduced state exhibits an unusual split Soret band at 360 and 450 nm in the presence of CO. These bands have been classified as a unique hyperporphyrin (HP) spectrum resulting from a mixture of two transitions: sulfur p′ → porphyrin π^* and porphyrin $\pi \to \pi^*$ (p′ being one of two lone-pair sulfur orbitals).[3] Characterization of this thiolato–ferrous heme–CO axial coordination mode was achieved with chemical model complexes by Stern and Peisach,[4] followed by Collman and Sorell,[5] Chang and

Dolphin,[6] and Caron et al.[7] These model complexes played an important role in showing that a cysteinyl thiolato ligand is present in the ferrous P-450–CO complex.

On the other hand, similar unusual HP spectra due to bis(thiolato)iron and cobalt protoheme complexes provided by exogenous thiolato binding at the sixth axial position of Fe(III)[8,9]

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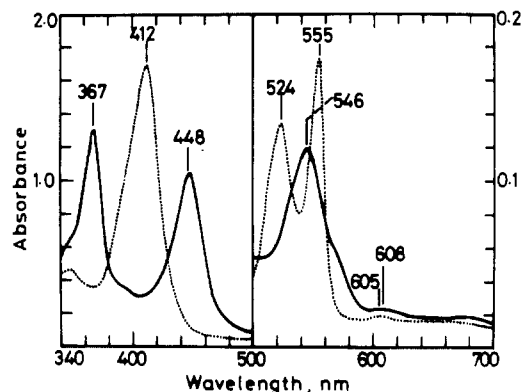§ Technology University of Nagaoka.

Figure 1. Hyperporphyrin spectrum of the $Rh^{III}(OEP)$-TGE-Bu_4NOH system in acetone at room temperature. To a mixture (—) of Rh^{III}-(OEP)Cl (0.25 mM in acetone, 0.1 mL), TGE (0.05 M in acetone, 0.25 mL), and acetone (2.65 mL) was added Bu_4NOH (1 M in methanol, 1 μL) under air at room temperature (20 °C) (···).

and Co(III)-substituted[10] P-450 confirmed that the axial fifth ligand on the heme in the enzymes is also a cysteinyl thiolato ligand. Similar HP spectra were found by Sono et al. for thiolato adducts of ferric chloroperoxidase, supporting the presence of an exogenous cysteinato ligand on the heme in the enzyme.[11] Model chemical complexes exhibiting HP spectra have been constructed[12-15] to support the result obtained for P-450 and chloroperoxidase. The occurrences of these unusual spectra, exhibiting split Soret bands, with peaks in the near-UV 350–380-nm region and in the visible 400–480-nm region, are currently limited to the transition-metal porphyrins having 3d electrons, such as those of iron,[12,13] cobalt,[14] and chromium.[15] Therefore, we sought another unusual HP spectrum for a transition-metal porphyrin complex having 4d electrons. We report here the detection and characterization of the stable HP spectra for bis(thiolato)-Rh^{III}(OEP)[16] complexes having aliphatic and aromatic thiol compounds as the thiolato ligands. During the investigations, we also found the generation of the free superoxide anion, coupling with the formation of the HP spectra. On the basis of ESR spectroscopy, a possible mechanism for the generation of the superoxide anion by a bis(thiolato)-Rh^{III}(OEP) complex will be presented.

Experimental Section

Materials. Rh^{III}(OEP)Cl[16] was prepared and purified according to literature procedures.[17] Fe^{III}(OEP)Cl and Co^{II}(OEP) complexes were gifts from Dr. Sugimoto of Osaka City University. All thioglycolate

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(16) Abbreviations: Rh^{III}(OEP)Cl, (octaethylporphyrinato)rhodium(III) chloride; TPP, tetraphenylporphyrinato; PPIX, protoporphyrinato IX; TG, thioglycolate; TGE, TG ethyl ester; TGnO, TG n-octyl ester; TGOD, TG octadecyl ester; DTT, dithiothreitol; Bu_4NOH, tetrabutylammonium hydroxide; ESR, electron spin resonance; Li-TCNQ, tetracyanoquinodimethane Li^+ salt.

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Table I. Hyperporphyrin Spectra of $Rh^{III}(OEP)$-TGE-Bu_4NOH Systems in Various Solvents[a]

solvent	abs max, nm (ϵ, mM^{-1} cm^{-1})			
	λ_1	normal	λ_2	
acetone	367 (83)		448 (60)	546 (12)
benzene	368 (77)		449 (66)	546 (13)
CH_3CN	364 (78)		442 (63)	542 (12)
CCl_4	365 (78)		445 (65)	544 (12)
$CHCl_3$	363 (66)		439 (74)	541 (16)
CH_2Cl_2	365 (71)	410 (42)	423 (62)	544 (13)	551 (13)
THF	369 (82)	399 (41)	451 (56)	547 (14)
DMSO	367 (40)	409 (112)	446 (24)	521 (13)	553 (21)
MeOH	354 (44)		428 (82)	535 (15)	564 (8)
EtOH	357 (50)		431 (80)	537 (14)	565 (6)
1-PrOH	358 (52)		433 (77)	539 (14)	566 (7)
1-BuOH	358 (55)		433 (76)	540 (14)	567 (6)
1-OcOH	360 (56)		436 (71)	539 (14)	566 (6)

[a] Concentrations of the compounds are the same as for Figure 1.

esters,[16] thionalide (TN), 4-chlorothiophenol (4-Cl-TP), 3,4,5-trichlorothiophenol (3,4,5-Cl-TP), 2-, 3-, and 4-toluenethiol (2-Me-TP, 3-Me-TP, and 4-Me-TP), 2,3,5,6-tetrafluorothiophenol (2,3,5,6-F-TP), thiosalicylic acid (TSA), and tetrabutylammonium hydroxide (Bu_4NOH) (10% in methanol) were products of Tokyo Chemical Industry. 2-Mercaptoacetanilide (MAA), ethyl 3-mercaptopropionate (EMP), methyl 3-mercaptopropionate (MMP), 2- and 3-chlorothiophenol (2-Cl-TP and 3-Cl-TP), 3,4-, 2,5-, and 2,6-dichlorothiophenol (3,4-Cl-TP, 2,5-Cl-TP, and 2,6-Cl-TP), 2,3,4,5,6-pentachlorothiophenol (2,3,4,5,6-Cl-TP), 2-, 3-, and 4-bromothiophenol (2-Br-TP, 3-Br-TP, and 4-Br-TP), and 4-fluorothiophenol (4-F-TP) were obtained from Aldrich Chemical Co. All solvents, acetone, benzene, acetnitrile (CH_3CN), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), carbon tetrachloride (CCl_4), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), methyl ethyl ketone (MEK), ethyl acetate (EtAc), pyridine (py), methanol (MeOH), ethanol (EtOH), 1-butanol (1-BuOH), 1-propanol (1-PrOH), 1-octanol (1-OcOH), were of special reagent grade from Wako Pure Chemicals and were distilled before use.

Spectrophotometric Measurements. Electronic absorption spectra were recorded under air on a Union Giken SM-401 high-sensitivity spectrometer at 20 °C. ESR measurements were carried out on a JES-FE1XG or JES-ME-3X (X-band) spectrometer with 100-kHz modulation at 77 K; these spectrophotometers were calibrated with a Takeda Riken TR 5212 frequency counter. Li-TCNQ ($g = 2.00252$) or $CrCl_3$ ($g = 1.9807$) and Mn(II) in MgO were used as standards. All samples for electronic absorption and ESR spectra were prepared under air at 20 °C.

Results and Discussion

Formation of Hyperporphyrin Spectra. Addition of Bu_4NOH to a mixture of $Rh^{III}(OEP)Cl$ and TGE in benzene under aerobic conditions resulted in the appearance of a new split Soret band, with peaks at 367 and 448 nm, concomitant with an absorption band at 546 nm (Figure 1).[18] The apparent half-life of this new spectrum under air was over 30 min at the concentration ratio of TGE/Rh(OEP)Cl $\geq$ 100, monitored by each split Soret band. This spectrum is similar to those of the cobalt-substituted P-450cam–DTT complex (375, 467, and 573 nm)[10] and (TGE-S$^-$)$_2$-Co(PPIX) complex (372, 465, and 574 nm).[14c] Very similar spectra have previously been reported for the bis(thiolato)–iron-(III),[12,13] bis(thiolato)–cobalt(III),[14] and bis(thiolato)–chromium(III)[15] porphyrin complexes and the thiolato adduct complexes of native P-450cam in the oxidized form.[8,9] These unusual split Soret bands for the bis(thiolato)–metalloporphyrin complexes, as well as the well-known ferrous P-450–CO complex, were assigned to thiolato S p → porphyrin π^* charge-transfer transitions, which mix with the porphyrin $\pi \rightarrow \pi^*$ transition.[3] Therefore, on the basis of these observations and results, it was considered that the present new spectrum showing the intense split Soret band is attributable to a kind of hyperporphyrin (HP) spectrum due to the formation of a bis(thiolato)–Rh^{III}(OEP) complex.

Solvent Effects on the Formation of the Hyperporphyrin Spectra. In order to characterize the HP spectrum due to a bis(thiola-

(18) Rh^{III}(OEP)Cl shows absorption maxima at 403, 519, and 552 nm in benzene. Addition of Bu_4NOH to Rh^{III}(OEP)Cl solution causes few spectral changes, showing the maxima at 405, 519, and 552 nm.

Table II. Hyperporphyrin Spectral Properties of Bis(thiolato)-Metalloporphyrin Complexes in Acetone[a]

porphyrin	central metal	bis(thiolato) ligand	λ_1	normal	λ_2		
					abs max, nm (ϵ, mM^{-1} cm^{-1})		
OEP	Rh(III)	TGE	367 (79)		448 (60)	546 (12)	608 (1)
		TGnO	366 (87)	409 (30)	447 (47)	549 (13)	
		TGOD	366 (73)	408 (37)	447 (50)	523 (13)	553 (13)
		MMP	371 (100)	409 (34)	455 (54)	522 (8)	553 (14)
		EMP	371 (94)	408 (33)	457 (50)	523 (8)	553 (14)
		MAA	365 (77)	410 (33)	442 (67)	544 (18)	
		TN	364 (77)		440 (80)	543 (18)	564 sh
OEP[b]	Co(III)	TGE	368 (81)	387 (62)	462 (32)	509 (13)	549 (22)
OEP[b]	Fe(III)	TGE	360 (59)		445 (33)	545 (13)	630 (10)

[a] Concentrations of the compounds are the same as for Figure 1. [b] The data refer to ref 14a and 14c.

to)-Rh^{III}(OEP) complex, the solvent effects on the formation of this unique spectrum were studied (Table I). The split Soret band showed absorption maxima at 363–369 and 439–448 nm in organic solvents except alcohols, being blue-shifted about 10 nm in both bands, compared with those observed for the corresponding bis-(thiolato)-Co^{III}(TPP)[13d,14c] and -Fe^{III}(TPP) complexes.[13d] In most solvents examined, the HP spectra were stable, showing no spectral changes for at least 30 min. However, the HP spectrum in THF was unstable, the half-life of the spectrum for the (TGE-S$^-$)$_2$-Rh^{III}(OEP) complex was estimated to be 4 min. In several solvents such as CH$_2$Cl$_2$, THF, DMSO, and MEK, the normal absorption band (~410 nm) concomitant with the HP spectra was observed, indicating that small portions of Rh^{III}(OEP) are not in the bis-(thiolato) form.

A characteristic feature was observed when alcohols were used as solvent. In bis(thiolato) complexes such as those of Fe^{III}(TP-P),[13d] Co^{III}(TPP),[14c] and Cr^{III}(TPP)[15] reported previously, an alcohol molecule may be bound to an axial position of the metalloporphyrins by substitution for an axial tholato ligand, forming

$$\text{thiolato(S}^-\text{)} - \text{metal} - \overset{\displaystyle |}{\underset{\displaystyle R}{O}} H$$
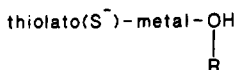
axial coordination modes. In the case of the Rh^{III}(OEP) systems, however, no substitution of a thiolato ligand by an alcohol was indicated. In alcohol solvents, formations of HP spectra similar to those found in other solvents were apparently observed. Moreover, the split Soret bands, with peaks at λ_1 and λ_2, were correlated linearly with dielectric constants[19] of the alcohols (Figure 2). As the polarity of the solvent decreases, the split Soret band red-shifts. In addition, the HP spectra formed in those alcohols were also stable, the half-lives of the spectra being about 30 min.

Effects of Axial Thiolato Ligands on Hyperporphyrin Spectra. As the HP spectrum obtained with the (TGE-S$^-$)$_2$-Rh^{III}(OEP) complex was stable for over 30 min, the effect of thiolato ligands on the formation of HP spectra was studied in two solvents, acetone and benzene. In Table II, the HP spectra for several types of thiol compounds are summarized. The esters of thioglycolate gave almost the same split Soret band with peaks at 367–368 and 446–448 nm, but as the ester moiety became longer, the normal absorption band at about 410 nm remained. On the other hand, when MMP or EMP, in which a methyl group is introduced to TGE, was used, the split Soret band red-shifted about 4–9 nm.

Aromatic thiol compounds formed stable HP spectra in both acetone and benzene solvents under air (Table III). In order to see whether the split Soret band correlates with the chemical structure of aromatic thiol compounds, the shift values (Δ_1 or Δ_2) of each split Soret band from those observed with thiophenol were plotted against the Hammett σ values[20] for the one and two
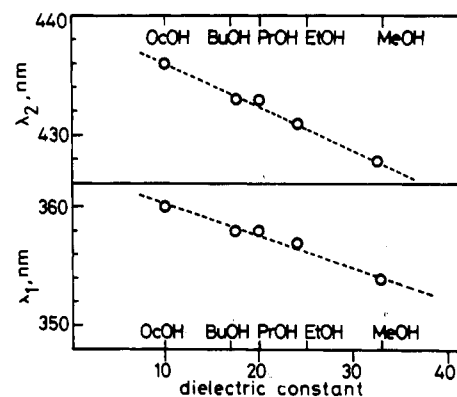

Figure 2. Relationship between the split Soret band (λ_1 and λ_2) of hyperporphyrin spectra of the (TGE-S$^-$)$_2$-Rh^{III}(OEP) complex and dielectric constants of alcohols as solvent. The values of the dielectric constants were obtained from ref 19, and the split Soret bands for the complexes refer to Table I.
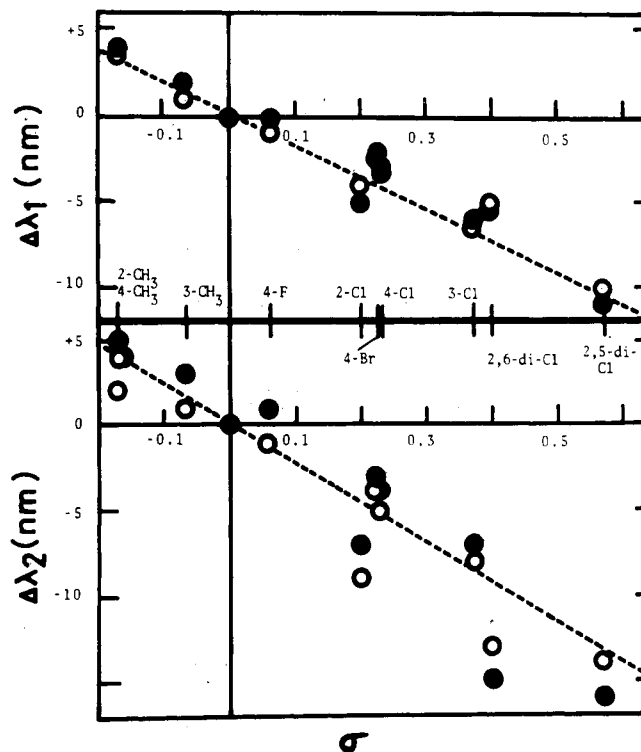

Figure 3. Hammett relationship for the split Soret band of hyperporphyrin spectra of bis(thiolato)-Rh^{III}(OEP) complexes for thiophenol derivatives in acetone and benzene solvents. The Δ_1 and Δ_2 values refer to those in Table III. ● and ○ represent the values in acetone and benzene solvent, respectively.

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substituents of thiophenol derivatives (Table III and Figure 3). As seen in Figure 3, a good linear relationship at each Soret peak was found, indicating that the positions of the absorption bands

Table III. Hyperporphyrin Spectral Properties of Bis(thiolato)–Rh^{III}(OEP) Complexes of Various Aromatic Thiol Compounds in Acetone and Benzene Solvents and Relationship between Hammett's Constants (σ) and the Split Soret Band of Hyperporphyrin Spectra of the Complexes^a

thiolato ligand	solvent^b	λ_1	normal	λ_2		Hammett's const (σ)	$\Delta\lambda_1$, nm	$\Delta\lambda_2$, nm
2-Me-TP	a	383 (82)		464 (32)	553 (11)	−0.17	+4	+6
	b	385 (80)		459 (35)	551 (12)		+4	+2
3-Me-TP	a	381 (81)		461 (37)	553 (11)	−0.069	+2	+3
	b	382 (80)		458 (41)	551 (12)		+1	+1
4-Me-TP	a	383 (79)		462 (33)	553 (11)	−0.17	+4	+4
	b	385 (86)		461 (38)	554 (16)		+4	+4
TP	a	379 (89)	405 (44)	457 (44)	559 (15)	0.0	0	0
	b	381 (91)		457 (52)	550 (15)		0	0
2-Br-TP	a	374 (77)		451 (50)	546 (13) 572 (5)	+0.21	−5	−7
	b	376 (68)		450 (52)	546 (13) 571 (5)		−5	−7
3-Br-TP	a	374 (85)		449 (50)	548 (12)	+0.391	−5	−8
	b	377 (71)		450 (58)	547 (13)		−6	−7
4-Br-TP	a	370 (106)		454 (48)	549 (13)	+0.227		−4
	b	378 (81)		452 (50)	548 (14)		−3	−5
4-F-TP	a	379 (90)	405 sh	459 (39)	552 (13)	+0.062	0	+1
	b	380 (70)	408 sh	456 (35)	550 (11)		−1	−1
2-Cl-TP	a	374 (78)		449 (50)	527 (9)	+0.20	−5	−9
	b	377 (74)		450 (54)	547 (14)		−4	−7
3-Cl-TP	a	373 (66)		451 (38)	547 (10)	+0.373	−5	−7
	b	375 (84)		449 (60)	546 (15)		−6	−8
4-Cl-TP	a	377 (88)	407 (51)	449 (43)	522 (9) 552 (16)	+0.232	−2	−9
	b	377 (76)	413 (43)	450 (52)	552 (16)		−4	−7
3,4-Cl-TP	a	373 (110)		449 (72)	546 (13) 572 (3)			
	b	375 (103)		447 (77)	545 (14) 569 (4)			
2,5-Cl-TP	a	368 (96)		442 (76)	543 (13) 569 (4)	+0.573	−11	−16
	b	371 (94)		443 (84)	543 (14) 569 (5)		−10	−12
2,6-Cl-TP	a	−		443 (76)	545 (14) 572 (5)	+0.40		−15
	b	376 (86)		444 (79)	545 (14) 572 (5)		−5	−13
3,4,5-Cl-TP	a	−		441 (79)	542 (14) 569 (5)			
	b	−		442 (85)	543 (15) 569 (5)			
2,3,4,5,6-TP	a	−		436 (92)	543 (15) 572 (8)			
	b	373 (110)		437 (100)	545 (17) 572 (9)			
TSA	a	363		430	536 565			
	b	363		431	535 566			
2,3,5,6-F-TP	a	363 (78)		434 (100)	540 (17) 569 (9)			
	b	365 (76)		436 (62)	540 (16) 569 (8)			

^{a} Final concentrations of Rh^{III}(OEP)Cl, the thiol compound, and Bu$_4$NOH were 8.3 μM, 4.2 mM, and 0.33 mM, respectively. ^{b} a and b represent acetone and benzene, respectively.

Table IV. ESR Parameters for the Superoxide Anion Detected at 77 K in Various Systems

system	solvent	$g_\parallel$	$g_\perp$
Rh^{III}(OEP)–TGE–Bu$_4$NOH	benzene	2.088	2.006
	THF	2.096	2.009
Co^{III}(TPP)–TGE–Me$_4$NOH^a	CH$_2$Cl$_2$	2.084	2.006
Fe^{III}(TPP)–TGE–Me$_4$NOH^b	CH$_2$Cl$_2$	2.088	2.007
KO$_2$^{c}	DMSO	2.087	2.007

^{a} Reference 14a. ^{b} Reference 14b. ^{c} Reference 22.

for the split Soret peaks depend on the magnitude of the positive or negative inductive effect of the substituents of thiophenol.

Generation of the Superoxide Anion by a Bis(thiolato)–Rh^{III}-(OEP) Complex. The ESR spectra of the (TGE-S$^-$)$_2$–Rh^{III}(OEP) complex prepared under air in benzene were measured at 77 K, while the concentration ratio of TGE to Rh^{III}(OEP)Cl was varied. The ESR spectrum of the complex prepared at a ratio of 5–100 had no observable signal due to any Rh(II) species, but g values ($g_\perp$ = 2.006 and $g_\parallel$ = 2.088 at 77 K) provided evidence for the formation of free superoxide anion. A similar ESR signal due to the superoxide anion was detectable in THF solvent ($g_\perp$ = 2.009 and $g_\parallel$ = 2.096 at 77 K) (Table IV). These g values are very similar to those obtained by using the model complexes[13d,14a,b,21] for the thiolato adduct complexes of P-450 and the KO$_2$–crown ether system.[22] The present results suggest that in the complex prepared at a concentration range of TGE to Rh^{III}(OEP) of 5–100,
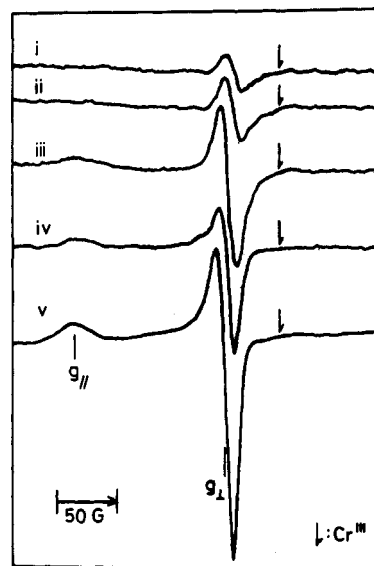

Figure 4. Generation of the superoxide anion by the Rh^{III}(OEP)–TGE–Bu$_4$NOH system in THF. A mixture of Rh^{III}(OEP)Cl (0.5 mM in benzene, 0.25 mL), TGE (10 mM in THF, 0.1 mL), THF (0.11 mL), and Bu$_4$NOH (80 mM in methanol, 0.04 mL) was prepared in vacuo at room temperature (20 °C), and the ESR spectra was measured at 77 K (i). Oxygen was bubbled through the solution at room temperature and the ESR spectrum was measured at 77 K (ii). This procedure was repeated (iii–v), and the superoxide anion was detected after four times.

Rh^{III}(OEP) is reduced by the axial thiolato ligand, followed by reaction with molecular oxygen to form the superoxide anion.

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(22) Bray, R. C.; Mautner, G. N. In *Superoxide and Superoxide Dismutases*; Michelson, A. M., McCord, J. M., Fridovich, I., Eds.; Academic: New York, 1977; pp 61–75 and references therein.

Scheme I. Possible Reaction Mechanism for Superoxide Generation by a Bis(thiolato)rhodium(III) Octaethylporphyrin[a]
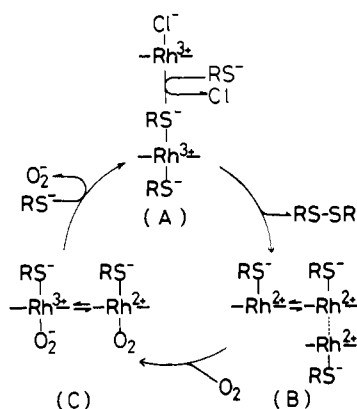
[a] –Rh– represents rhodium(III) octaethylporphyrin.

In order to gain insight into the reaction mechanism between $(TGE-S^-)_2Rh^{III}(OEP)$ and molecular oxygen, the ESR spectra of the complex prepared in benzene and THF in vacuo were measured by repeating freeze–thawing under molecular oxygen (Figure 4). As seen in Figure 4, the generation of free superoxide anion was found for the complexes on gradual exposure to oxygen. On the other hand, when $Rh^{II}(OEP)$, prepared from $Rh^{III}(OEP)Cl$ on a zinc mirror, was added to the TGE solution, followed by Bu_4NOH in vacuo,[23] no ESR signals due to Rh(II) species were detectable.

Possible Reaction Mechanism for Generating the Superoxide Anion in a Bis(thiolato)–Rh^{III}(OEP) Complex in the Presence of Molecular Oxygen. On the basis of electronic absorption and ESR

spectral studies on a bis(thiolato)–Rh^{III}(OEP) complex in the presence of molecular oxygen in organic solvents, we speculate that the reaction mechanism for generating the superoxide anion in the complex is as shown in Scheme I, considering the mechanism for the corresponding Co^{III}-[14a,b] and Fe^{III}(TPP)[13d] complexes. A is a new hyperporphyrin spectral complex having a bis(thiolato)–Rh^{III}(OEP) coordination mode, deduced by electronic absorption spectrometry. B is a speculative and ESR-silent complex. C is also a speculative complex, being very unstable with a very short half-life. The generation of superoxide anion will continue until the available thiolato ligand is oxidized to the disulfide form in the system. We are now conducting studies to establish the structures and physicochemical natures of the complexes proposed in Scheme I.

Conclusion. Characteristic hyperporphyrin spectral features that appear upon bis(thiolato) ligation to Rh^{III}(OEP)Cl showed a marked similarity to those observed for thiolato adducts of P-450cam, cobalt-substituted P-450cam, and bis(thiolato)–Fe^{III}(TPP), –Co^{III}(TPP), and –Cr^{III}(TPP) complexes. The bis(thiolato)–Rh^{III}(OEP) complexes containing various types of aliphatic and aromatic thiol compounds were stable at room temperature under air, their half-lives being over 30 min. The positions of the characteristic split Soret band correlated linearly with the dielectric constants of alcohols as solvent and with the Hammett σ values of the substituents of thiophenol derivatives as axial ligands on Rh^{III}(OEP) in both acetone and benzene solvents. The unusual HP spectra with metalloporphyrins having 4d and 5d electrons are already known for antimony(III) and bismuth(III) porphyrins.[3a] However, the present bis(thiolato)–Rh^{III}(OEP) complex is the first example for HP spectra due to the formation of the coordination mode by bis(thiolato) metalloporphyrins having 4d electrons. Under the conditions observed for the formation of a hyperporphyrin spectrum, the generation of free superoxide anion was detectable at 77 K by ESR spectrometry. On the basis of the results, a possible reaction mechanism generating the superoxide anion by a bis(thiolato)–Rh^{III}-(OEP) complex is proposed.

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(23) The zinc mirror, Rh^{III}(OEP)Cl (0.5 mM in benzene, 0.25 mL), TGE (10 mM in acetone, 0.1 mL), and Bu$_4$NOH (80 mM in methanol, 0.04 mL) were prepared in four cuvvettes connected to an anaerobic ESR tube.

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Vanadium(V) Oxyanions. Interactions of Vanadate with Cyclic Diols and Monosaccharides

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^{51}V nuclear magnetic resonance studies have shown that the vanadium(V) oxyanion, vanadate, reacts with *cis*- and *trans*-1,2-cyclohexanediols and the glucose, galactose, and mannose methyl pyranosides to give a variety of products including vanadate esters, divanadate esters, both binuclear mixed and symmetrical pentacoordinate anhydrides, and in the case of the methyl α- and β-galactopyranosides a previously unobserved binuclear product. The equilibrium constant for formation of esters with hydroxyls of the six-membered rings was found to be comparable to that observed for the formation of ethyl vanadate. In the case of the cyclohexanediols the formation of the pentacoordinate products was more highly favored for the *cis*-diol as compared to the *trans*-diol by a factor of about 10. For the glucosides only a very small proportion of pentacoordinate products was formed and then only for the α-anomer, while the formation of this product with the other monosaccharides was comparable to that of the cyclohexanediol system. A mixed pentacoordinate/tetrahedral binuclear vanadate product was formed in the presence of methyl galactopyranoside but not with methyl mannopyranoside. A third binuclear species was also observed. The latter product was formed with incorporation of two methyl galactopyranosides but was found to readily incorporate a third.

Introduction

The interactions of vanadate with carbohydrates have been a topic of developing interest since it was first proposed that oxovanadium complexes with uridine formed and that these products acted as transition-state analogues for enzymic reactions of phosphorylated uridine.[1] Subsequent nuclear magnetic resonance

(NMR) studies[2,3] supported this conclusion, and X-ray and neutron diffraction studies showed the proposed transition-state geometry in a vanadate/uridine/ribonuclease complex.[3,4] Further

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