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Communications

An Unusual Hyperporphyrin Spectrum for a Bis(thiolato)-Chromium(III) Tetraphenylporphyrin Complex

Sir:

Cytochrome P450 in the reduced state exhibits unusual split Soret bands at 360 and 450 nm in the presence of CO. These bands have been assinged to a unique hyperporphyrin spectrum resulting from a mixture of two transitions: sulfur p′ → porphyrin π^* and porphyrin $\pi \rightarrow \pi^*$ (p′ being one of two lone-pair sulfur orbitals).[1] Characterization of the thiolato–ferrous heme–CO coordination mode was achieved with chemical model complexes by Stern and Peisach,[2] followed by Collman and Sorrell,[3] Chang and Dolphin,[4] and Caron et al.[5] These model complexes convinced the researchers in the field of cytochrome P450 that a cysteinyl thiolato ligand is present in the ferrous P450–CO complex. On the other hand, similar unusual hyperporphyrin spectra due to bis(thiolato)iron and -cobalt protoheme complexes provided by thiolato binding to Fe(III)[6,7] and Co(III)-substituted[8] cytochrome P450 complexes also played an important role in confirming the axial fifth ligand to the heme in the enzymes as being a cysteinyl thiolato ligand. Model chemical complexes exhibiting hyperporphyrin spectra[9-12] have been constructed to support this idea in cytochrome P450. The occurrence of these unusual hyperporphyrin spectra, exhibiting split Soret bands in the near-UV 350–380-nm region and in the visible 400–480-nm region, is currently limited to iron and cobalt porphyrins. Recent increased interests in chromium chemistry[13] and biochemistry[14] prompted us to investigate chromium porphyrin complexes with thiolato ligands. We report here the detection and characterization of a stable hyperporphyrin spectrum due to bis(thiolato)–Cr^{III}TPP[15] complexes using thioglycolate esters as the thiolato ligand.

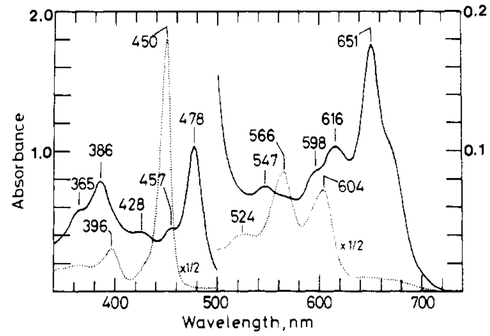

Figure 1. Electronic absorption spectra of bis(thiolato)–Cr^{III}TPP complexes at room temperature. To a mixture (- -) of Cr^{III}(TPP)Cl (0.25 mM dissolved in $CHCl_3$, 0.1 mL), TGE (0.125 M in acetone, 0.1 mL), and $CHCl_3$ was added 2.8 mM Me_4NOH (1 M in methanol; 5 μL) (—) under air at room temperature (20 °C).

Experimental Section. Cr^{III}(TPP)Cl was prepared and purified according to literature procedures.[16] Thioglycolate esters, thionalide, *p*-chlorothiophenol and Me_4NOH (10% in methanol) were products of Wako Pure Chemical Industry or Tokyo Chemical Industry. Mercaptoacetanilide was obtained from Aldrich Chemical Co. All solvents were distilled before use. All samples for electronic absorption and ESR spectra were prepared under air at 20 °C. Electronic absorption spectra were recorded under air on a Union Giken SM 401 high-sensitivity spectrometer at 20 °C. ESR measurements were carried out by using a JES-ME-3X spectrometer with 100 kHz field modulation at 77 K. DPPH (g = 2.0036) and Mn(II) in MgO were used as standards.

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(15) Abbreviations: Cr^{III}(TPP)Cl, chloro(*meso*-tetraphenylporphyrinato)-chromium(III); TG, thioglycolate; TGE, thioglycolate ethyl ester; TGbB, TG *n*-butyl ester; TGEH, TG 2-ethylhexyl ester; TGnO, TG *n*-octyl ester; TGiO, TG isooctyl ester; TGOD, TG octadecyl ester; MPM, β-mercaptopropionate methyl ester; MPE, β-mercaptopropionate ethyl ester; MAA, mercaptoacetanilide; TN, thionalide; *p*-CTP, *p*-chlorothiophenol; Me_4NOH, tetramethylammonium hydroxide; DPPH, 1,1-diphenyl-2-picrylhydrazyl (free radical); ESR, electron spin resonance.

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Table I. Hyperporphyrin Spectra of Bis(thiolato)-Metalloporphyrin Complexes[a]

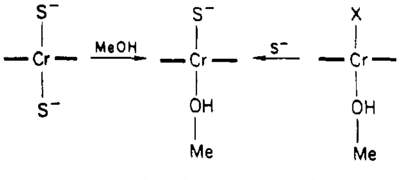
metal porphyrin	thiolate ligand												
$Cr^{III}TPP$ ($CHCl_3$)	TGE	λ	365	386	428	457	478	547		598	616	651	668 sh
		ε	70	94	51	55	124	8		11	12	22	13
	TGnB	λ	364	385	427	454	477	548	567	597 sh	615	651	666 sh
		ε	70	93	53	67	124	7	7	9	12	20	12
	TGEH	λ	364	385	430	454	477	547	566	599	615	650	666 sh
		ε	69	92	54	72	119	8	7	10	12	19	12
	TGnO	λ	366	386	429	455	478	548	566	600	615	652	670
		ε	70	92	53	70	120	8	7	10	12	19	11
	TGiO	λ	365	385	428	454	477	548	565 sh	599 sh	615	651	667 sh
		ε	72	95	54	72	125	8	8	11	13	20	12
	TGOD	λ	364	385	427	456	477	547	564	599 sh	614	650	665 sh
		ε	70	92	53	67	123	8	7	10	12	20	12
	MPM	λ	365	390	439	455	479			596	620	653	673
		ε	29	42	25	35	40			4	5	7	5
	MPE	λ	367	391	439	455	480			597	623	653	674
		ε	30	47	30	41	42			5	6	8	5
	MAA	λ	362	386	420	458	476	543		599 sh	611	647	
		ε	51	59	40	41	89	6		7	8	16	
	TN	λ	361	386	420 sh	457	475	546		594 sh	612	648	
		ε	54	59	39	75	86	7		8	8	17	
	p-CTP	λ		409		454	477	549	567	600	613	654	
		ε		64		64	46	6	7	7	8	12	
$Fe^{III}TPP$ (acetone)	TGE	λ	375		428	460		554 sh	576 sh		626		
		ε	84		51	82					5		
$Co^{III}TPP$ (acetone)	TGE	λ	381	411 sh		472					611 sh	660	
		ε	118			66						11	

[a] sh = absorption shoulder. λ in nm; ε in mM^{-1} cm^{-1}.

Results and Discussion. Aerobic addition of Me_4NOH to a mixture of $Cr^{III}(TPP)Cl$ and TGE in $CHCl_3$ at room temperature (20 °C) resulted in formation of an intensely green solution showing split Soret bands mainly at 386 and 478 nm concomitant with bands at 616 and 651 nm (Figure 1).[17] As judged by the spectral pattern, the green solution appears to contain small amounts of several species of the complex. To clarify this point we are now trying to isolate the green complex from the solution. The green solution was very stable under these conditions, showing no spectral changes over a period of at least 2 h, which was monitored by the intensities of the two Soret peaks. When KOH (in methanol) was used in place of Me_4NOH, the same spectrum was obtained but changed gradually with a half-life of about 60 min. Very similar spectra have previously been reported for the bis(thiolato)-iron(III)[9,10] and bis(thiolato)-cobalt(III)[11,12] porphyrin complexes and the thiolato adduct complexes of Fe(III)-[6,7] and Co(III)-substituted[8] cytochrome $P450_{cam}$. These unusual two split Soret bands for the bis(thiolato)-metalloporphyrin complexes as well as for the ferrous P450-CO complex were assigned to be due to thiolato S p → porphyrin π^* charge-transfer transitions, which mix with the porphyrin $\pi \rightarrow \pi^*$ transitions.[1] Therefore, it may be considered at present that the green color showing the intense split Soret bands is mainly attributed to the bis(thiolato)-$Cr^{III}TPP$ complex.

The ESR spectrum of the corresponding green complex in the frozen state clearly showed the occurrence of $Cr^{III}TPP$ species (Figure 2), demonstrating no valence change of chromium by reduction or oxidation during the complex formation. This spectrum is very similar to the ESR spectra of the six-coordinate $Cr^{III}TPP$ complexes reported previously.[16] As seen in Figure 2, remarkable changes in ESR spectra of $Cr^{III}TPP$ complexes were not observed, depending on the type of axial ligands such as chloride, hydroxide, thiol, and thiolate. This trend is similar to the result with low-spin hemin complexes, where large differences in the ESR *g* values were not observed.[10] The detailed ESR analysis on the $Cr^{III}TPP$ complexes will be reported in a future communication.

The assignment of the green complex as the source of the unusual hyperporphyrin spectrum was further supported by ligand exchange reactions, as suitably used in the structural analysis for the active site of P450 by chemical model compounds.[10] When the hyperporphyrin complex was titrated with methanol, new absorption bands at 453 (Soret band), 566, and 610 nm and four isosbestic points at 416, 464, 540, and 613 nm were observed, indicating the methanol-induced spectral change is reversible and the two chemical species are in equilibrium. On the other hand, when $Cr^{III}(TPP)Cl$[19] in the presence of methanol and Me_4NOH was titrated with TGE, the same new spectrum (absorption maxima 453, 566, and 610 nm) was observed with concomitant formation of a small portion of the hyperporphyrin spectrum. The new complex with absorption bands at 453, 566, and 610 nm was concluded to have a thiolato ligand at the fifth position and a methanol oxygen at the sixth position of $Cr^{III}TPP$ and to be stabilized with this coordination structure. The reaction sequence can be depicted as follows:



S^-: ROOC—CH_2—S^-
X^-: Cl^- or OH^-

Thus the green spectrum with split Soret bands at 386 and 478 nm was tentatively characterized as a hyperporphyrin spectrum due to the bis(thiolato)-$Cr^{III}TPP$ complex. Electronic spectral properties of the hyperporphyrin complexes with several thioglycolate esters are summarized in Table I, as are the results on the corresponding Fe(III)[10] and Co(III)[11] complexes. On the basis of the apparent half-life of the complexes monitored by the main Soret absorption bands characteristic of the hyperporphyrin spectra of bis(thiolato)-CrTPP, -FeTPP, and -CoTPP complexes,[10,11] the stability of the complexes are judged to be in the order Cr > Fe > Co.

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(17) No spectral changes were observed when TGE was added to Cr^{III}(TPP)Cl in $CHCl_3$. Although the spectrum of $Cr^{III}(TPP)Cl$ itself is classified as a d-type hyperporphyrin spectrum by Gouterman,[18] the present hyperporphyrin spectrum of the bis(thiolato)-$Cr^{III}TPP$ complex is classified as an unusual one like that of ferrous cytochrome P450-CO complex.

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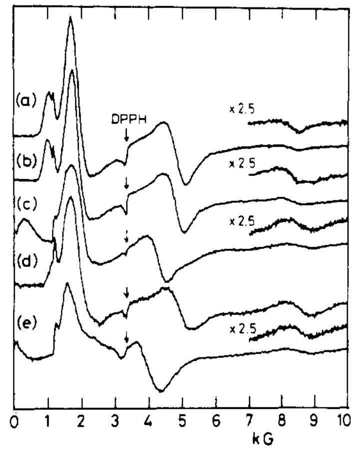

Figure 2. ESR spectra of $Cr^{III}TPP$ complexes at 77 K: (a) $Cr^{III}(TPP)Cl$ in $CHCl_3$, (10 mM; total volume 0.2 mL); (b) mixture used for curve a plus TGE (1 M; total volume 0.2 mL); (c) mixture used for curve b plus Me_4NOH (1 M; 60 μL); (d) mixture used for curve a plus Me_4NOH (1 M; 60 μL); (e) mixture used for curve a plus methanol (60 μL).

The results presented here provide not only a synthetic method of a new type of chromium(III) porphyrin complex but also an insight into the axial coordination mode of Cr(III)-substituted cytochrome P450 if it is prepared.

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Redox Asymmetry and Metal–Metal Coupling in Pyrazine-Bridged Ruthenium Dimers

Sir:

Elucidation of the nature and extent of electronic coupling in mixed-valence dimers continues to present a challenging theoretical and experimental problem.[1-3] The pyrazine-bridged diruthenium decaammine species $[Ru(NH_3)_5]_2pyz^{5+}$ (the Creutz–Taube ion[4]) presents a particularly intriguing case since it does not appear to fall squarely into either the predominantly valence-localized Robin and Day class II category or the fully delocalized class III category.[5,6]

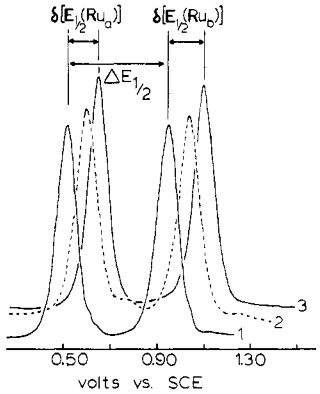

Figure 1. Differential pulse polarograms and identification of experimental quantities: (1) Creutz–Taube ion, $[(NH_3)_5Ru]_2pyz^{4+/5+/6+}$; (2) *trans*-$pyRu_b(NH_3)_4(pyz)Ru_a(NH_3)_5^{4+/5+/6+}$; (3) *trans*-2,6-$Me_2pyzRu_b(NH_3)_4(pyz)Ru_a(NH_3)_5^{4+/5+/6+}$. Measurements made in 0.1 M $(TEA)PF_6$ in acetonitrile at 2 mV/s with a 10-mV pulse amplitude and 0.2-s drop time.

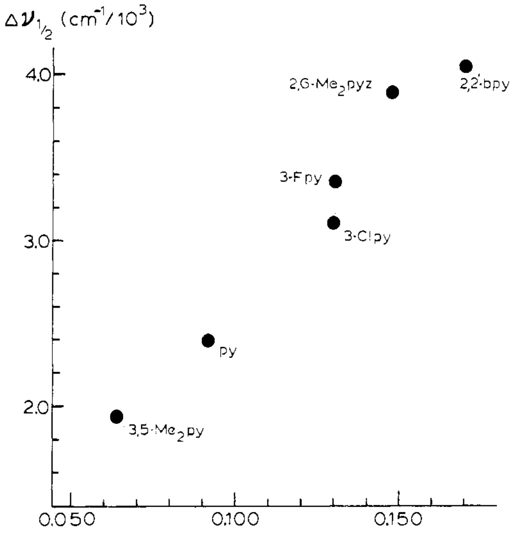

Figure 2. $\Delta\nu_{1/2}$, bandwidth at half-maximum for intervalence-transfer band vs. $\delta[E_{1/2}(Ru_b)]$, shift in second redox wave relative to Creutz–Taube ion second wave: 3,5-Me_2py = 3,5-dimethylpyridine; py = pyridine; 3-Cl-py = 3-chloropyridine; 2,6-Me_2pyz = 2,6-dimethylpyrazine; 2,2'-bpy = 2,2'-bipyridine.

We wish to report here on a novel approach to the investigation of metal–metal coupling in mixed-valence dimers and its preliminary application to a series of pyrazine-bridged species related to the Creutz–Taube ion. Experimentally the approach involves the systematic introduction of redox asymmetry into a dimer using a *trans*-$LRu(NH_3)_4$ fragment on one end of the molecule, where L is varied over different nitrogen heterocycles so as to "tune" the redox potential of that end. Variations of the redox potential at the *other* end are then observed, and their magnitude is taken as being indicative of the extent of coupling between the sites. This technique has been applied previously to the case of metal–ligand interactions in complexes where a discrete ligand-localized reduction wave is observable such as *trans*-$LRu^{II}(NH_3)_4(pyd)^{3+}$, where pyd = *N*-methyl-4,4'-bipyridinium or *N*-methyl-4-cyanopyridinium, and in complexes such as $M(bpy)_2L_2^{2+}$, where M = Ru, Os and bpy = 2,2'-bipyridine.[7,8]

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(9) We note the identification of the first and second redox waves with $E_{1/2}(Ru_a)$ and $E_{1/2}(Ru_b)$ is probably without rigorous meaning at the narrow, $\Delta\nu_{1/2}$ end of the series since these dimers are substantially class III in nature.