The incomplete extinction of luminescence upon oxidation shows that some emission comes from molecules that are not electroactive, but the depth of modulation implies that the oxidized electroactive centers have a large quenching radius. If these centers are spread evenly over the surface, they would be separated from each other, on the average, by 50–80 Å. Thus any point of excitation in a dip-coated layer on BPPG would be within 40 Å of such a quenching center. It is entirely reasonable that an exciton resulting from light absorption would be quenched over such a distance by one-step resonance transfer. There is also the prospect of exciton migration among unoxidizable molecules. To the extent that this process occurs, the need for a strong resonance interaction between exciton and quenching center would be reduced. These considerations lead to a realization that none of the modulated luminescence may actually arise from electroactive sites.

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Porphyrins. 44.[1] Electronic States of Co, Ni, Rh, and Pd Complexes

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Abstract: Iterative extended Hückel (IEH) calculations are presented with the aim of understanding the near-UV, visible, and near-IR absorption spectra and the emission properties of Co, Rh, Ir, Ni, Pd, and Pt porphyrins. UV–visible spectra are reviewed for 30 such complexes; new near-IR spectra are presented for Co^{II}, Ni^{II}, and Pd^{II} complexes of octaethyl- and tetraphenylporphyrin (OEP and TPP). We also report that three Co^{III} complexes and one Pt^{IV} complex show no emission. While the calculations do not well predict shifts of the visible spectra, they are able to explain quenching by transitions at lower energy than the usual ring phosphorescent state $^3T_1(\pi,\pi^*)$ and fluorescent state $^1Q(\pi,\pi^*)$. These states are as follows: (d,π^*) in Co^{I} porphyrin; (π,d) in Co^{II}, Ni^{IV}, and Pd^{IV} porphyrins; and $^3(d,d)$ in Co^{III} and Ni^{II} porphyrins. No quenching states are predicted for the strongly phosphorescent Rh^{III} and Pd^{II} porphyrins. In the near-IR absorption, bands identified as transitions to (d,π^*) were earlier reported for Co^{I} porphyrin; in this paper we report bands in Co^{II} porphyrins corresponding to $^2(\pi,d)$. We also locate absorptions in the near-IR corresponding to the $^2T_1(\pi,\pi^*)$ state of Co^{II}(OEP) and the $^3T_1(\pi,\pi^*)$ states of Pd^{II}(OEP), Pd^{II}(TPP), and Pt^{IV}(TTP)Cl$_2$ [TTP = mesotetratolylporphyrin]. We have not yet located $^1(d,d)$ bands in Co^{III} or Ni^{II} porphyrins; nor $^1(\pi,d)$ in Co^{III} and Pd^{IV} porphyrins; nor $^1(d,\pi)$ in Ni^{II} porphyrins. The $^1(\pi,d)$ state of Ni^{IV} and Pd^{IV} porphyrins is expected to the red of 1100 nm, the limit of our current studies; the other states may be found in the near-IR with careful study but perhaps are hidden under the $^1Q(\pi,\pi^*)$ bands.

The enzymatically important Fe porphyrins exhibit very dramatic spectral changes as a function of ligands and oxidation state,[2] which reflect the changing electronic structure of their ground and excited states. The porphyrin complexes of the congener metals, Ru and Os, also show dramatic spectral changes with change of ligands. The systematics of the spectral changes in complexes Os(OEP)LL′ have been discussed by the authors[3] with some comparisons given to Fe and Ru.[4] The iterative extended Hückel (IEH) calculations used in those papers provide a good qualitative picture for the electronic structure of these complexes: The smaller d orbitals of Fe have a relatively small crystal field splitting between the lower energy orbitals d_{xy}, d_{xz}, d_{yz} and the higher energy orbitals d_{z^2}, $d_{x^2-y^2}$; hence ligands on Fe porphyrins can give rise to low, intermediate, and high spin complexes by modulating this splitting.[5] For the Ru and Os porphyrins, the crystal field splitting of the 4d and 5d orbitals is much larger, so that d_{z^2} and $d_{x^2-y^2}$ are never populated. Nonetheless ligands can strongly influence the absorption and emission spectra and the redox properties by shifting the energy of the filled d_{xy}, d_{xz}, d_{yz} orbitals relative to the energy of the four orbitals of the ring [$a_{1u}(\pi)$, $a_{2u}(\pi)$, $e_g(\pi^*)$],[6] which are responsible for the lower energy porphyrin excited states.

In this paper we use the same model to consider the electronic structure of Co, Ni, Rh, and Pd porphyrins. Since the calculated structures for Ru and Os porphyrins were quite similar,[4] we expect a similarity between Rh and Ir porphyrins and between Pd and Pt porphyrins, and we have not done calculations on the heavier metals.

In the complexes considered here the metals have configuration d^6, d^7, and d^8. An experimental generality we wish to address concerns the fact that the emission properties do not depend on electron configuration. The known published studies can be summed up as follows: (i) Co and Ni complexes show no emission whether d^6, d^7, or d^8; (ii) Rh as d^6 and Pd and Pt as d^8 show strong phosphorescence and weak fluorescence.[6–9] [Ir as d^6 has had little

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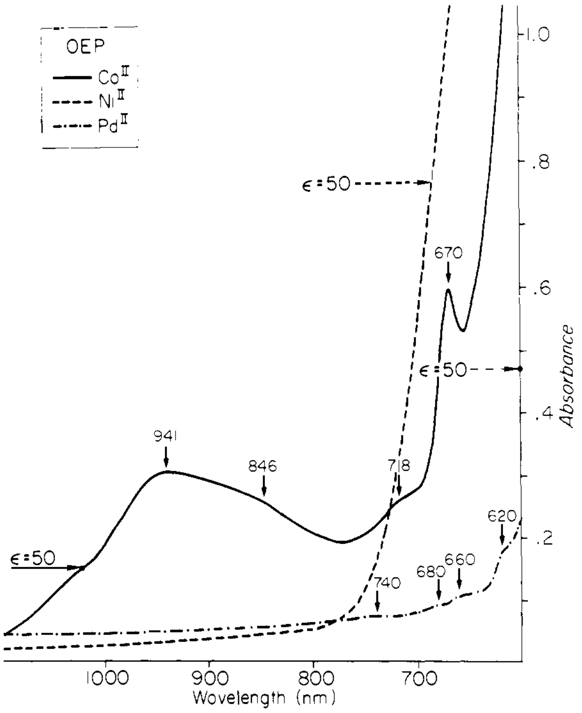

Figure 1. Near-IR absorption spectra of $\mathrm{Co^{II}(OEP)}$ (—) 3.0×10^{-4} M, $\mathrm{Ni^{II}(OEP)}$ (---) 1.5×10^{-3} M, and $\mathrm{Pd^{II}(OEP)}$ (···) 9.3×10^{-4} M, all in $\mathrm{CH_2Cl_2}$ in a 10-cm cell at room temperature.

study but is reported to phosphoresce.[6]] Our paper here entends earlier negative emission studies[7] to give negative reports on the emission of the three $\mathrm{Co^{III}}$ complexes and the one $\mathrm{Pt^{IV}}$ complex. Our experimental studies also include a $\mathrm{Ni^{IV}}$ species; however, since that compound was not well characterized chemically, this report must be considered tentative. We carry out IEH calculations that attribute lack of emission to low energy excited states of either (d,d), (π,d), or (d,π*) character, depending on the complex. In an attempt to observe these states we report the near-IR absorption spectra for several Co, Ni, Pd, and Pt porphyrins; but only in the $\mathrm{Co^{II}}$ complexes have we found clear charge-transfer aborption bands. We predict which molecules should show near-IR bands not yet observed and characterized.

Experimental Data and IEH Parameters

Emission. The emission apparatus was basically the same as described earlier.[4,10] In general we believe that when we report that a compound shows "no emission" and hence is "radiationless",[6] it means that the quantum yield for emission is below 10^{-4}.

In our current studies we examined for emission at 77 K the following complexes: $\mathrm{Co^{III}(Etio)Br(NH_3)}$, $\mathrm{KCo^{III}(OEP)(CN)_2}$, $\mathrm{Ni^{IV}(OEP)(Br_x)_2}$ $x = 1$ or 3), and $\mathrm{Pt^{IV}(TTP)Cl_2}$. [Porphyrin and solvent abbreviations can be found in footnotes to Table I.] The first three, which were studied in EPA, were supplied by Prof. David Dolphin of the University of British Columbia; the platinum complex, which was studied in acetone, was supplied by Prof. J. W. Buchler of the Technische Hochschule, Darmstadt. Details of our purification techniques are given elsewhere.[11] Although several weak emissions were observed, they were shown by excitation spectra to come from impurities, and the main species are "ratiationless". [Since the IEH calculations predict quenching of $\mathrm{Pd^{IV}}$ complexes by the (π,d) charge transfer state, a phosphorescing species prepared by the Dolphin research group and thought to be $\mathrm{Pd^{IV}(OEP)(Br_x)_2}$ ($x = 1$ or 3) was reexamined by mass spectra and found to be ring brominated $\mathrm{Pd^{II}}$ porphyrin. The $\mathrm{Pt^{IV}(TTP)Cl_2}$ sample, in contrast, showed clear emission from a $\mathrm{Pt^{II}(TTP)}$ impurity, as established by excitation studies. This emission confirms that the apparatus was working well (always a question in a negative experiment) and adds support to the identification of the main species as a $\mathrm{Pt^{IV}}$ complex.]

Table I. Near-UV-Visible Absorption Peaks of Co, Rh, Ir, Ni, Pd, and Pt Porphyrins[a-d]

compound[c]	absorption $B(0,0)$, $Q(0,1)$, $Q(0,0)$ (nm), solvent	ref[f]
	A. Octaethylporphyrin	
$\mathrm{Co^{II}(OEP)}$	384, 520, 550, $\mathrm{CH_2Cl_2}$	7, 12
$\mathrm{Co^{III}(OEP)NH_3(Br)}$	411, 525, 559, EPA[b]	*
$\mathrm{KCo^{III}(OEP)(CN)_2}$	411, 528, 560, EPA[b]	*
$\mathrm{Ni^{II}(OEP)}$[d]	392, 516, 551, $\mathrm{CH_2Cl_2}$	7, 12
$\mathrm{Ni^{IV}(OEP)(Br_x)_2}$[e]	407, 525, 565, EPA[b]	*
$\mathrm{Rh^{III}(OEP)Cl(H_2O)_2}$	403, 520, 554	13
$\mathrm{Rh^{III}(OEP)CH_3}$	396, 512, 544, $\mathrm{CHCl_3}$	14
$\mathrm{Pd^{II}(OEP)}$	390, 512, 544, $\mathrm{CH_2Cl_2}$	8, 12, *
$\mathrm{Ir^{III}(OEP)CH_3}$	389, 501, 529, $\mathrm{CHCl_3}$	16
$\mathrm{Ir^{III}(OEP)Cl(CO)}$	402, 516, 547, $\mathrm{CHCl_3}$	16
$\mathrm{Pt^{II}(OEP)}$	382, 503, 536, $\mathrm{C_6H_6}$	15
	B. Octaalkylporphyrins[a-c]	
$\mathrm{Co^{II}(Etio)}$	408, 526, 558, EPA	7, *
$\mathrm{Ni^{II}(Etio)}$[d]	392, 517, 553, triethylamine	7
$\mathrm{[Rh^{III}(Etio)(DMA)_2]Cl}$	397, 514, 546, $\mathrm{CH_2Cl_2}$	9
$\mathrm{Pd^{II}(Etio)}$	389, 510, 544, EPAF[b]	7
$\mathrm{Pt^{II}(Etio)}$	378, 500, 536, EPAF[b]	7
$\mathrm{Co^{II}(Meso)}$	396, 518, 549, dioxane	17
$\mathrm{Co^{III}(Meso)(OH)}$	419, 530, 562, pyridine	17
$\mathrm{Rh^{III}(MesoDEE)(Cl)}$	397, 512, 544 (568 sh), $\mathrm{CCl_4}$	18
$\mathrm{Ir^{III}(MesoDEE)(Cl)}$	398, 515, 548 (~600 sh), $\mathrm{CCl_4}$	18
$\mathrm{Ir^{III}(HematoDEE)(Cl)}$	401, 515, 544 (484 sh), $\mathrm{CHCl_3}$	18
	C. Tetraphenyl- and Tetratolylporphyrin[a-c]	
$\mathrm{Co^{II}(TPP)}$	404, 530, -, $\mathrm{CH_2Cl_2}$	7, 19
$\mathrm{Ni^{II}(TTP)}$	415, 527, -, $\mathrm{CH_2Cl_2}$	15
$\mathrm{Rh^{II}(TPP)}$	418, 531, 568 (601), $\mathrm{CHCl_3}$	20
$\mathrm{Pd^{II}(TPP)}$	418, 524, 554, $\mathrm{C_6H_6}$	7, 21
$\mathrm{Pd^{II}(TTP)}$	416, 523, 556, $\mathrm{CH_2Cl_2}$	15
$\mathrm{Pd^{IV}(TTP)Cl_2}$	423, 534, 564, $\mathrm{CH_2Cl_2}$	22
$\mathrm{Pt^{II}(TPP)}$	403, 510, 539, $\mathrm{C_6H_6}$	7, 21
$\mathrm{Pt^{II}(TTP)}$	403, 510, 539, $\mathrm{CH_2Cl_2}$	22
$\mathrm{Pt^{IV}(TTP)(Cl)_2}$	420, 537, 575, $\mathrm{CH_3Cl_2}$	22

[a] Room-temperature absorption. [b] Solvent abbreviations: EPA: ethyl ether, isopentane, ethanol (5:5:2). EPAF: diethyl ether, isopentane, dimethylformamide, ethanol (12:10:6:1). PMA: poly(methyl methacrylate) (solid). MeTHF: methyltetrahydrofuran. [c] Porphyrin skeleton abbreviations: OEP (octaethylporphyrin); Etio (etioporphyrin); TPP (tetraphenylporphine); TTP (mesotetra-*p*-tolylporphyrin; Meso (mesoporphyrin IX); MesoDEE (mesoporphyrin IX diethyl ester); HematoDEE (hematoporphyrin diethyl ester). [d] For the effect of strong bases on Ni porphyrins see ref 23. [e] Species not well characterized. [f] An asterisk indicates experimental work performed in this study. The data taken either on a Cary 14 or an a Varian Super-Scan 3.

Near-UV-Visible Absorption. Table I reports the absorption peaks of several Co, Rh, Ir, Ni, Pd, and Pt porphyrins. All these spectra are blue shifted with respect to the spectra of closed d-shell porphyrins; i.e., they have *hypso* spectra.[6] The shifts observed among these compounds will be discussed after we present the IEH calculations.

Near-IR Absorption. Spectra were taken at room temperature on a Cary 14 spectrophotometer. Spectra for $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, and $\mathrm{Pd^{II}}$ complexes are shown in Figures 1 and 2 for OEP and TPP, respectively. $\mathrm{Co^{II}(OEP)}$ shows clear peaks at 941 and 718 nm with $\epsilon \sim 100\ \mathrm{M^{-1}\ cm^{-}}$; $\mathrm{Co^{II}(TPP)}$ shows one at 856 nm with $\epsilon \sim 75\ \mathrm{M^{-1}\ cm^{-1}}$. Since $\mathrm{Co^{II}}$ porphyrins show reversible oxidation to $\mathrm{Co^{III}}$ and reduction to $\mathrm{Co^{I}}$,[24] it is not immediately clear whether these bands are (π,d) or (d,π*). Since the bands are moderately intense and since $a_{2u}(\pi) \rightarrow a_{1g}(d_{z^2})$ is allowed whereas $d \rightarrow e_g(\pi^*)$ is forbidden as $g \rightarrow g$, the former seems the more likely interpretation. This view also agrees with some preliminary solvent shift data.[25] In addition to these broad bands we observe sharper

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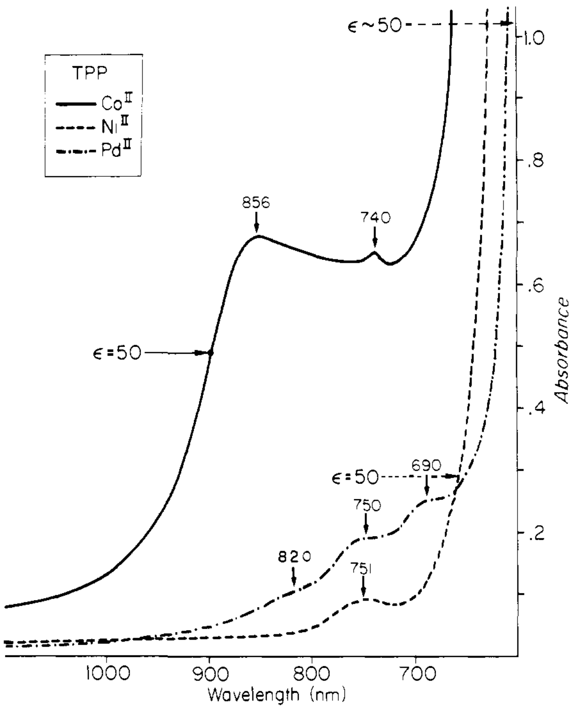

Figure 2. Near-IR absorption spectra of Co^{II}(TPP) (—) 9.7×10^{-4} M, Ni^{II}(TPP) (---) 5.7×10^{-4} M, and Pd^{II}(TPP) (-·-) 2.1×10^{-3} M, all in CH_2Cl_2 in a 10-cm cell at room temperature. The extinction coefficient for Pd^{II}(TPP) is estimated from Pd^{II}(OEP)/Ni^{II}(OEP) ~ Pd^{II}(TPP)/Ni^{II}(TPP).

Table II. Basis Set Exponentials (au^{-1})

	s	p	d	
Co	1.43	1.43	3.22	4s, 4p, 3d
Ni	1.47	1.47	3.39	
Rh	1.59	1.59	2.96	5s, 5p, 4d
Pd	1.63	1.63	3.13	

bands at 670 nm [Co(OEP)] and 740 nm [Co(TPP)]. The former is clearly real, and we identify the excited state as the lowest energy triplets, $^2T_1(\pi,\pi^*)$.[26] The 740-nm band, if real, may be of the same origin.

Ni^{II}(OEP) shows an unstructured tail absorbance that falls from $\epsilon \sim 50$ M^{-1} cm^{-1} to the base line between 685 and 785 nm. Ni^{II}(TPP) falls similarly between 660 and 830 nm. In addition, Ni^{II}(TPP) shows a small peak at 751 nm. Throughout this same region the Pd^{II} complexes show less absorption, with $\epsilon < 25$ M^{-1} cm^{-1} for $\lambda > 600$ nm in Pd^{II}(OEP) and for $\lambda > 625$ nm in Pd^{II}(TPP). Pd^{II}(OEP) shows a peak at 660 nm and Pd^{II}(TPP) shows one at 690 nm with $\Delta\epsilon \lesssim 3$ M^{-1} cm^{-1}, where $\Delta\epsilon$ is the rise above the tail absorbance. These two wavelengths correspond to the known triplet emission[7] and hence represent absorption to the $^3T_1(\pi,\pi^*)$ excited states. The weak peaks to the red of $^3T_1(\pi,\pi^*)$ we consider artifacts, since they have lower energy than the known phosphorescence origin. The similarity of the artifactual 750-nm peak of Pd^{II}(TPP) with the unknown 751-nm band of Ni^{II}(TPP) suggests that the latter is also an artifact. The same may hold for the 740-nm band of Co^{II}(TPP).

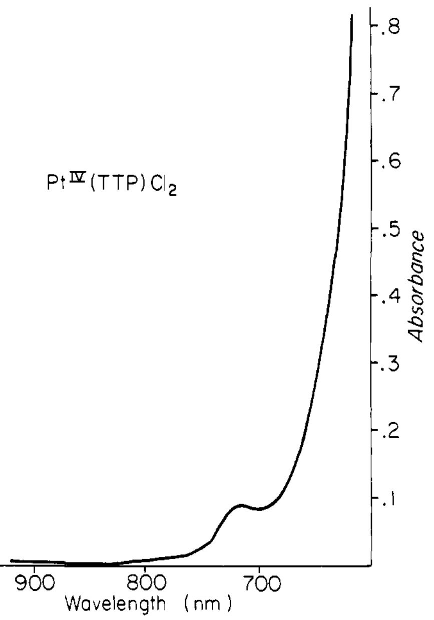

Figure 3. Near-infrared absorption of $Pt(TTP)Cl_2$ in acetone at room temperature.

Table III. Valence Orbital Ionization Energies (eV)

$M \rightarrow M^+ + (e)$		$M^+ \rightarrow M^{2+} + (e)$	
Co			
$I_p = 7.86$		$I_p = 17.05$	
$d^8s \rightarrow d^8$	7.45	$d^7s \rightarrow d^7$	16.40
$d^8p \rightarrow d^8$ $d^7sp \rightarrow d^7s$	4.23	$d^7p \rightarrow d^7$	11.40
$d^9 \rightarrow d^8$ $d^8s \rightarrow d^7s$	7.18	$d^8 \rightarrow d^7$	8.20
Ni			
$I_p = 7.633$		$I_p = 18.15$	
$d^9s \rightarrow d^9$	7.55	$d^8s \rightarrow d^8$	16.92
$d^9p \rightarrow d^9$	3.95	$d^8p \rightarrow d^8$	11.50
$d^{10} \rightarrow d^9$ $d^9s \rightarrow d^8s$	7.90	$d^9 \rightarrow d^8$	18.80
Rh			
$I_p = 7.46$		$I_p = 18.07$	
$d^7s^2 \rightarrow d^7s$ $d^8s \rightarrow d^8$	7.41	$d^7s \rightarrow d^7$	15.75
$d^8p \rightarrow d^8$	3.80	$d^7p \rightarrow d^7$	10.83
$d^9 \rightarrow d^8$ $d^8s \rightarrow d^7s$ $d^8p \rightarrow d^7p$	10.08	$d^8 \rightarrow d^7$ $d^7s \rightarrow d^6s$ $d^7p \rightarrow d^6p$	21.90
Pd			
$I_p = 8.33$		$I_p = 19.42$	
$d^8s^2 \rightarrow d^8s$ $d^9s \rightarrow d^9$ $d^8sp \rightarrow d^8p$	7.28	$d^8s \rightarrow d^8$	16.04
$d^9p \rightarrow d^9$ $d^8sp \rightarrow d^8s$	4.56	$d^8p \rightarrow d^8$	10.86
$d^{10} \rightarrow d^9$ $d^9s \rightarrow d^8s$ $d^96s \rightarrow d^86s$ $d^9p \rightarrow d^8p$ $d^95d \rightarrow d^85d$	11.10	$d^9 \rightarrow d^8$ $d^8s \rightarrow d^7s$ $d^86s \rightarrow d^76s$ $d^8p \rightarrow d^7p$	23.25

We also examined the near-IR absorbance of Pt^{IV}(TTP)Cl$_2$. The spectrum shows a clear absorption band at 715 nm (Figure 3). Since this is 3400 cm^{-1} to the red of the $Q(0,0)$ absorption,

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Table IV. Geometries (Å)

M(P)L(L^1)	metal-N$_p$^{a}	metal-CN, -CO, -Cl	metal-py
Co^{III}(P)CN(py)	1.979	1.86	1.95
Co^{III}(P)Cl(py)	1.95	2.369	1.95
Ni^{II}(P)	1.95		
Ni^{IV}(P)Cl$_2$	1.95	2.60	
Rh^{III}(P)CN(py)	2.038	1.95	2.11
Rh^{III}(P)Cl(py)	2.038	2.36	2.11
Pd^{II}(P)	2.01		
Pd^{IV}(P)Cl$_2$	2.01	2.86	

^{a} Metal-N$_p$ distance for Co^I(P), Co^{II}(P) same as for Co^{III}(P), similarly Rh^I(P), Rh^{II}(P) same as for Rh^{III}(P).

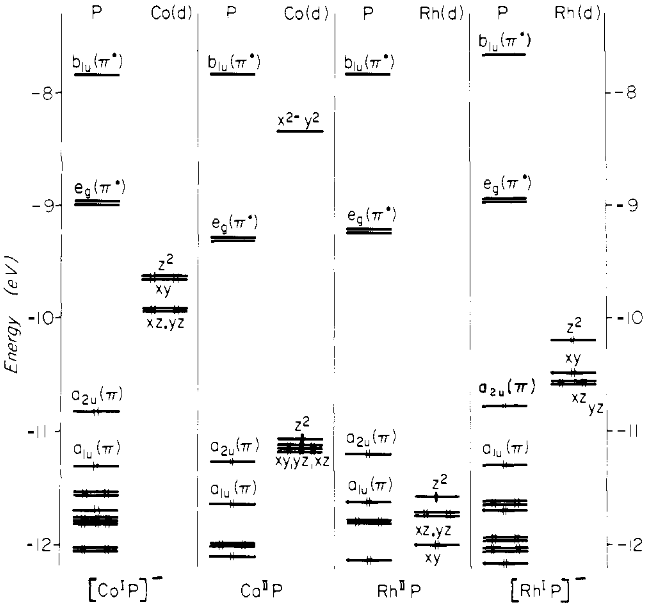

Figure 4. Molecular orbital energy levels for Co^I, Co^{II}, Rh^I, and Rh^{II} complexes. The MO's are grouped as P, M(d), depending on whether the charge density is largest on the porphine ring or on the metal.

a typical value for the energy gap between the lowest excited singlet and lowest excited triplet states in porphyrins, the band is probably $^3T_1(\pi,\pi^*)$. There is, in addition, a very weak broad absorption from 740 to 820 nm. This may be the predicted $^1(\pi,d)$ transition (see below) but then again may be an artifact. The near-IR absorption spectrum shows no other bands out to 1100 nm.

Iterative Extended Hückel (IEH) Method and Parameters. The IEH model was initially described by Zerner et al.[27,28] Our basis set exponentials (Table II) were obtained by the method of Cusachs et al.,[29] as was done for Fe, Ru, and Os.[3,4] Calculations on Co and Ni with use of Zerner exponentials[27] were also carried out; this parameter change did not produce any significant difference in the results. For Cl, the Zerner exponentials were used.[27]

The ionization potetials (Table III) for Co and Ni were those of Zerner,[27] while for Rh and Pd they were similarly calculated from the spectroscopic tables of Moore as for Ru and Os.[3,4] The Cl ionization potentials were obtained from the tables of Basch et al., as presented by McGlynn et al.[30]

The geometries were obtained from crystal structure studies or estimated from covalent radii and are given in Table IV. The orientation of the porphyrin molecules with respect to coordinate axes was such that the center of the coordinate system coincided with the center of the porphyrin plane and the nitrogens were on the x, y axes. All atoms were in the x, y plane. The calculations were done on the unsubstituted porphine (P) ring.

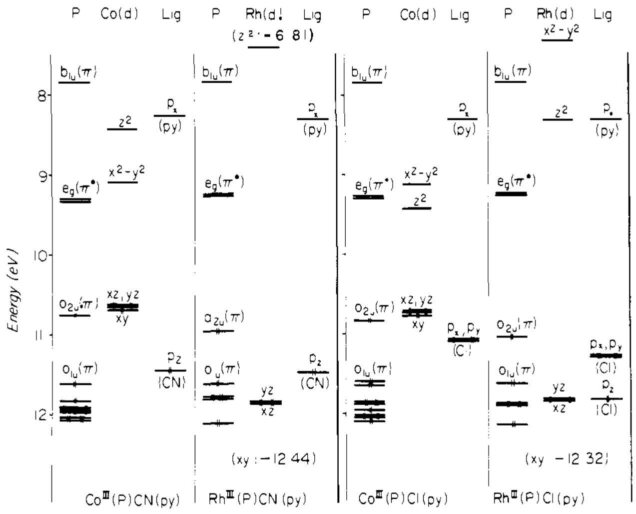

Figure 5. Molecular orbital energy levels for Co^{III} and Rh^{III} porphyrins. The MO's are grouped as P, M(d), L, depending on whether the charge density is largest on the porphine ring, metal, or ligand.

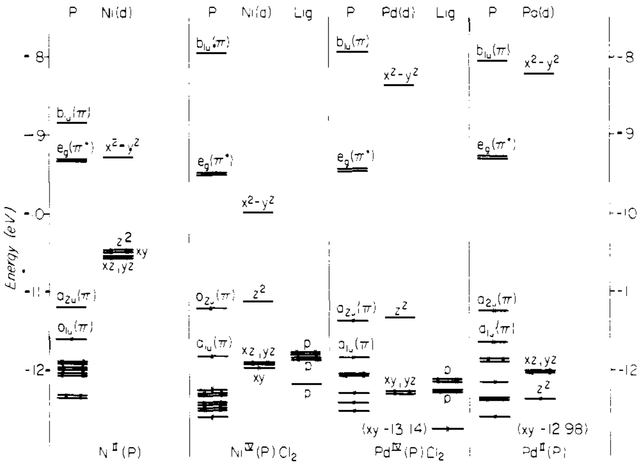

Figure 6. Molecular orbital energy levels for Ni^{II}, Ni^{IV}, Pd^{II}, and Pd^{IV} porphyrins. The MO's are grouped as P, M(d), L, depending on whether the charge density is largest on the porphine ring, metal, or ligand.

Table V. Charge Densities

compound	metal	l_1	l_2	porphine
Co(CN)(py)	0.309	−0.351	0.267	−0.225
Co(Cl)(py)	0.325	−0.398	0.327	−0.254
Ni(II)	0.251			−0.251
Ni(IV)Cl$_2$	0.365	−0.314	−0.314	0.263
Rh(III)CN(py)	0.250	−0.378	0.274	−0.146
Rh(III)Cl(py)	0.228	−0.358	0.356	−0.226
Pd(II)	0.109			−0.109
Pd(IV)Cl$_2$	0.257	−0.298	−0.298	0.339

Results and Discussion of Optical Data

Figure 4 shows the molecular orbital (MO) energy level diagram for Co^I, Co^{II}, Rh^I, and Rh^{II} porphyrins. Figure 5 gives them for Co^{III} and Rh^{III} porphyrins, showing the effect of having either Cl$^-$ or CN$^-$ as the counterion ligand. Figure 6 shows the MO levels for Ni^{II}, Ni^{IV}, Pd^{II}, and Pd^{IV} porphyrins. In the next sections we use these results to explain various aspects of the optical spectra. Calculated charge densities are given in Table V.

Near-UV-Visible Absorption. Naively, spectral shifts should correlate with the average energy, ΔE, for the two transitions $a_{1u}(\pi)$, $a_{2u}(\pi) \rightarrow e_g(\pi^*)$. We find that ΔE (Figures 4–6) varies

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from 1.90 to 2.19 eV along the series

$$\mathrm{Co^{III} < Ni^{IV} < Rh^{III} \lesssim Ni^{II} < Co^{II} \sim Pd^{II} \lesssim Pd^{IV} < Rh^{II}} \qquad (1)$$

As shown in Table I, the following relations occur among the lowest absorption band energies with change in oxidation state, change among congeners, and change between columns in the periodic table:

$\mathrm{Co^{III} < Co^{II}}$
$\mathrm{Ni^{IV} < Ni^{II}}$
$\mathrm{Pd^{IV} < Pd^{II}}$ (X)
$\mathrm{Rh^{II} < Rh^{III}}$ (X)

$\mathrm{Co^{III} < Rh^{III}}$
$\mathrm{Co^{II} < Rh^{II}}$ (X)
$\mathrm{Ni^{II} < Pd^{II}}$

$\mathrm{Co^{II} \approx Ni^{II}}$
$\mathrm{Rh^{III} \approx Pd^{II}}$ (X)

We have indicated by (X) those changes *not* predicted by the calculated ΔE given in (1) above. Failure of the IEH model to reproduce "delicate frequency trends of the visible bands" was pointed out by Zerner.[27]

However, the calculations strongly support the interpretation of the $\mathrm{Co^{I}}$ hyper spectra put forth by Kobayashi,[31] i.e., that the extra hyper bands arise from doubly excited states, $[d_\pi,\pi \rightarrow (\pi^*)^2]$. Figure 4 shows that such transitions should occur at low energy.

Emission. The lack of emission from Co complexes compared to the strong phosphorescence from $\mathrm{Rh^{III}}$ is well explained by the MO diagrams. Starting with Figure 4 we see that $\mathrm{Co^{I}}$ complex emission would be quenched by low-energy (d,π^*) charge-transfer (CT) transitions. For $\mathrm{Co^{II}}$ complexes, quenching would be due to low-energy (π,d) transition. Figure 4 suggests that similar quenching will occur for $\mathrm{Rh^{II}}$ porphyrin and, indeed, opens the possibility that there could be electronic isomers:

$$\mathrm{Rh^{II}(P) \rightleftharpoons Rh^{I}(P\cdot)}$$

The gap between d and π^* levels is calculated to be much higher in $\mathrm{Rh^{I}}$ porphyrin than in the $\mathrm{Co^{I}}$ complex. However, judging from a comparison to the (d,π^*) gaps of Ru and Os porphyrins, some of which emit and some of which do not, we predict that the $\mathrm{Rh^{I}}$ porphyrins will not show emission.

Considering Figure 5 we see that $\mathrm{Co^{III}}$ porphyrins are naively predicted to have (π,d), (d,π) and (d,d) transitions at about the same energy as the (π,π^*) transition. But it is long known that IEH calculations are not accurate for CT transitions. By using the redox information that $\mathrm{Co^{II}}$ is expected but not $\mathrm{Co^{IV}}$, we can eliminate (d,π) from consideration. Since the (d,d) exchange splitting between singlet and triplet should be larger than the (π,π^*) splitting, we expect the $^3(d,d)$ state to be the lowest energy excited state. Emission from this state might not be observed for several reasons: (i) the state may emit to the red of our detector; (ii) the state may decay radiationlessly; (iii) the state may decay by ligand loss. We see for $\mathrm{Rh^{III}}$ complexes that neither CT nor (d,d) transitions are expected to come between the lowest energy (π,π^*) states and the ground state. The same should be true for $\mathrm{Ir^{III}}$ complexes. Thus the calculations are consistent with the strong phosphorescence of $\mathrm{Rh^{III}}$ porphyrins.[9]

Reason for the contrast between the nonemitting $\mathrm{Ni^{II}}$ and the emitting $\mathrm{Pd^{II}}$ porphyrin appears in Figure 6. It can be seen that $\mathrm{Ni^{II}(P)}$ has low energy (d,d) transitions that are absent in Pd(P). The diagram predicts that the lowest excited state of four coordinate $\mathrm{Ni^{II}}$ porphyrins should be $^3(d_{z^2},d_{x^2-y^2})$. That this is the case has been shown by recent pulsed picosecond spectroscopy.[32,33] In basic solution $\mathrm{Ni^{II}}$ porphyrins become paramagnetic,[23] since in 6-coordination the d_{z^2} orbital rises in energy toward $d_{x^2-y^2}$. When $^3(d_{z^2},d_{x^2-y^2})$ becomes the ground state, the photokinetics are different[33] as expected from a detailed theoretical consideration of $\mathrm{Ni^{II}(P)}$ excited states.[34] While there is some evidence for $\mathrm{Pd^{II}}$ porphyrin complex formation with pyridine at low temperature,[7] such complexes are unlikely to be paramagnetic in view of the large gap between d_{z^2} and $d_{x^2-y^2}$ shown in Figure 6. For $\mathrm{Ni^{IV}}$ and $\mathrm{Pd^{IV}}$ porphyrins a low-energy (π,d_{z^2}) CT transition is expected that would quench any emission. This explains the lack of emission from the $\mathrm{Ni^{IV}(OEP)(Br_x)_2}$ [$x = 1$ or 3] and $\mathrm{Pt^{IV}(TTP)Cl_2}$ that we examined. [See above.]

Among the second- and third-row transition-metal complexes of group 8, many $\mathrm{Ru^{III}}$, $\mathrm{Os^{II}}$, $\mathrm{Os^{VI}}$, $\mathrm{Rh^{III}}$, $\mathrm{Pd^{II}}$, and $\mathrm{Pt^{II}}$ complexes show emission. The trends in emission yield and lifetime are brought about by two main factors: the d_π to $e_g(\pi^*)$ energy gap and the heavy-metal effect. Increase in d_π to $e_g(\pi^*)$ gap decrease d_π character introduced into $e_g(\pi^*)$ thus decreasing spin-orbit coupling and the radiative and radiationless rates between the singlet and triplet systems. This leads to increase in the small fluorescence yield and in the phosphorescence lifetime.[6] Thus, across the series we note an increase in fluorescence yield and phosphorescence lifetime, Ru < Rh < Pd. Down a column, Ru to Os, Rh to Ir, Pd to Pt, we observe the heavy-metal effect which increases the triplet to ground singlet radiative and radiationless decay rates, thus decreasing the phosphorescence lifetime. So far there is no good theory for the relative strengths of the radiationless vs. the radiative decay rates in these compounds, so that the variation in phosphorescence yield remains unexplained.

Near-IR Absorption. From Figure 4 we see that low-energy (d,π^*) transitions are predicted for $\mathrm{Co^{I}}$ porphyrins. In a detailed theoretical and experimental study, Kobayashi et al.[31] predict such transitions at 1000 and 600 nm and observe them in $\mathrm{[Co(TPP)]^-}$ at the latter wavelength. For $\mathrm{Co^{II}}$ porphyrins Figure 4 predicts an allowed $[a_{2u}(\pi) \rightarrow d_{z^2}]$ transition, and these are apparent in Figures 1 and 2. We know of no near-IR studies on $\mathrm{Rh^{I}}$ and $\mathrm{Rh^{II}}$ porphyrins, where analogous transitions to those of $\mathrm{Co^{I}}$ and $\mathrm{Co^{II}}$ are predicted.

Figure 5 shows no low-energy CT or (d,d) transitions for $\mathrm{Rh^{III}}$ porphyrins. However, for $\mathrm{Co^{III}}$ porphyrins the IEH calculations suggest the possibility of $^1(\pi,d)$ and $^1(d,d)$ transitions in the region of the lowest energy $^1Q(\pi,\pi^*)$ transitions. Figure 5 shows that the energy of $^1(\pi,d)$ and $^1(d,d)$ states will red drift with the ligand change CN → Cl.

From Figure 6 we see that in $\mathrm{Ni^{II}(P)}$ [as in $\mathrm{Co^{III}(P)}$] there would be transitions to $^1(d,d)$ and $^1(d,\pi^*)$ to the red of the $^1Q(\pi,\pi^*)$ transitons. Our spectra in Figures 1 and 2 show little evidence for these excited states. [We tend to view the 751-nm band of Figure 2 as an artifact.] Furthermore it is known that in $\mathrm{Ni^{II}(TPP)}$, metal and ring oxidation both occur at ~1.25 V and that there is and equilibrium between the electronic isomers.[25]

$$\mathrm{[Ni^{II}(TPP)]^+ \rightleftarrows [Ni^{III}(TPP\cdot)]^+}$$

Since we roughly correlate optical transition energy with difference in redox potentials,[36] we might expect the $^1(d,\pi^*)$ to lie under or in the tail of $^1Q(\pi,\pi^*)$, perhaps accounting for the strong tail in the near-IR absorption of $\mathrm{Ni^{II}}$ porphyrins compared to $\mathrm{Pd^{II}}$ porphyrins (Figures 1 and 2).

In the $\mathrm{Pd^{II}}$ complexes, no metal redox potential is known.[24] The complexes phosphoresce strongly; the IEH calculations predict (d,π^*) transitions at quite high energy. In agreement with this, no clear IR bands are observed, and we identify the weak absorptions at lower energy than the triplet state as impurities. The observed $\Delta\epsilon \sim 3\ \mathrm{M^{-1}\ cm^{-1}}$ for transitions to $^3T_1(\pi,\pi^*)$ would correspond to a radiative lifetime consistent with the observed phosphorescence lifetimes and quantum yields.[6,7]

In $\mathrm{Ni^{IV}}$ and $\mathrm{Pd^{IV}}$ porphyrins (Figure 6) a low-energy CT (π,d) band is predicted. This is in agreement with the lack of emission of $\mathrm{Pt(TTP)Cl_2}$ and $\mathrm{Ni(OEP)(Br_x)_2}$ [$x = 1$ or 3]. We examined the near-IR absorption spectra of the $\mathrm{Pt^{IV}}$ complexes (Figure 3). While a very weak broad band at ~780 nm may be this transition, the IEH calculations suggest that the transition lies to the red

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of 1100 nm, the limit of our studies.

Summary

In this paper we have used the IEH model to determine low-energy excited states of other than (π,π^*) origin in Co, Ni, Rh, and Pd porphyrins. [The congeners Ir and Pt should be similar to Rh and Pd, respectively.] The model does not accurately predict the transition energies from orbital energy differences, but it does provide a useful guide for explaining emission properties and also provides a basis for a serious search of the absorption spectra to the red of the lowest Q band for other than (π,π^*) transitions. We here summarize our conclusions and predictions by using P to stand for our calculations on porphine although the experiments could be on any porphyrin.

$\mathrm{Co^I(P)}$. Emission is quenched due to (d,π^*) transitions, which are identified in absorption. The doubly excited states $[d,\pi \rightarrow (\pi^*)^2]$ strongly affect visible spectra.[31]

$\mathrm{Rh^I(P)}$. There is very little study.[20] We predict no emission due to the (d,π^*) transitions. These should be at higher energy than in $\mathrm{Co^I(P)}$, so doubly excited states should not affect the visible absorption spectra as strongly.

$\mathrm{Co^{II}(P)}$. Emission is quenched due to (π,d) transitions, which are identified in the near-IR spectra with $\epsilon \sim 100\ \mathrm{M^{-1}\ cm^{-1}}$.

$\mathrm{Rh^{II}(P)}$. Recent work[37,38] has shown that the earlier reported species $\mathrm{Rh^{II}(TPP)}$[20] was actually $\mathrm{Rh(TPP)O_2}$ and that the species $\mathrm{Rh^{II}(TPP)}$ dimerizes. For the true monomer, which perhaps can be obtained under the right conditions, our calculations predict that there will be no emission due to a low-energy (π,d) excited state. It is even possible that, under the right conditions, this CT state might become the ground state; i.e., the molecule could exist as the electronic isomer $\mathrm{Rh^I(P\cdot)}$ rather than $\mathrm{Rh^{II}(P)}$.

$\mathrm{Co^{III}(P)}$. Emission is quenched by a low-energy $^3(d,d)$ state. We predict that this state may become manifest in picosecond flash spectroscopy. If sought, excited states $^1(d,d)$ and/or $^1(\pi,d)$ may be found in the near-IR absorption spectrum.

$\mathrm{Ni^{II}(P)}$. Emission is quenched by a low-energy $^3(d,d)$ state, which has become manifest in picosecond flash spectroscopy.[32,33] States $^1(d,d)$ and $^1(d,\pi^*)$ have not been observed in the near-IR absorption region, although we find a much stronger tail absorption than in $\mathrm{Pd^{II}(P)}$. Perhaps this tail may reveal $^1(d,d)$ and/or $^1(d,\pi^*)$ bands if observed in higher resolution conditions.

$\mathrm{Ni^{IV}(P)Cl_2}$ and $\mathrm{Pd^{IV}(P)Cl_2}$. Emission is quenched by low-energy (π,d) CT states. Transitions to such states should be sought in the absorption spectrum with $\lambda > 1100$ nm.

$\mathrm{Rh^{III}(P)X(py)}$ and $\mathrm{Pd^{II}(P)}$. [Here X is an anionic ligand.] No low-energy CT or (d,d) states are calculated, consistent with strong phosphorescence.[6-9] There are $\mathrm{Rh^{III}(P)}$ complexes that will probably not emit, e.g., Rh(P)NO and $\mathrm{Rh(P)O_2}$.[37,38] These would be quenched by low-energy CT transitions of (π,l_π^*) origin where l_π^* refers to the lowest empty orbital of the axial ligand. Such states are presumed responsible for the lack of emission from Ru(OEP)NO(OMe).[4] Indeed a band at 595 nm is reported in the absorption spectrum of $\mathrm{Rh(OEP)O_2}$[37,38] that may be of (π,l_π^*) origin.

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Interactions of the Aluminum(III) Ion in a Model Membrane System

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Abstract: The interactions of the aluminum(III) cation ($\mathrm{AlCl_3{\cdot}6H_2O}$) with the carbonylated headgroups of potassium dodecanoate contained in a bilayer membrane have been studied. It was found that under dilute conditions aluminum binds very strongly to the carboxylate groups as the $\mathrm{Al(OH)_4^-}$ ion but that this binding can be disrupted by the partial replacement of potassium dodecanoate with alkyltrimethylammonium. Disruption occurs only after about 25% of the dodecanoate is replaced by alkyltrimethylammonium indicating that aluminum causes the formation of an inhomogeneous bilayer, that is to say, regions from where cationic surfactant is excluded. No information concerning the size of the aggregates involved in such regions was obtained and they may simply be monomeric chelated aluminum complexes. When the bilayer is prepared from only dodecyltrimethylammonium bromide, the $\mathrm{AlCl_3{\cdot}6H_2O}$ can be added to very high concentrations with no significant effect on the bilayer stability indicating that this aluminum compound has no intrinsic disruptive effect other than that of chemical binding. Adding NaOH to this last mesophase eliminates the $\mathrm{Al(H_2O)_6^{3+}}$ resonance and provides a signal at 80 ppm corresponding to $\mathrm{Al(OH)_4^-}$.

The interactions of monatomic ions with the polar regions of amphiphilic compounds are of considerable interest in various areas of chemistry, biochemistry, and medicine. Nuclear magnetic resonance (NMR) studies of such interactions have tended to be restricted to the ions lithium, sodium, and potassium, although to a lesser extent the rubidium, cesium, and halide ions have been studied.[1-8]

One ion which has received little attention is the aluminum trivalent cation, $\mathrm{Al^{3+}}$. Although aluminum occurs abundantly in nature, it normally is present as chemical entities which are quite inert to further reactions. Aluminum has, however, been

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