Porphyrins. XXXI.[1] Chemical Properties and Electronic Spectra of d^0 Transition-Metal Complexes[2]

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Abstract: The octaethylporphin complexes of forms (OEP)MX_nL_m, (OEP)MO, and (OEP)M(O)X [M = Sc(III), Ti(IV), Zr(IV), Hf(IV), Nb(V), and Ta(V); X = univalent anion; L = neutral ligand] all show fluorescence and phosphorescence, as does the tetraphenylporphine complex (TPP)ScX. The fluorescence yields ($\phi_f \sim 0.2$) and phosphorescence lifetimes ($\tau_p \sim 400$ msec) of (OEP)ScX show very low spin-orbit coupling, i.e., no heavy-atom effect. The complexes of (OEP)ZrX_2L_2 and (OEP)HfX_2L_2 have fluorescence yields ($\phi_f = 0.02$ and 0.007), phosphorescence yields ($\phi_p = 0.096$ and 0.171), and phosphorescence lifetimes ($\tau_p = 65$ and 8.4 msec) that exhibit regular heavy-atom effects; the values for (OEP)TiO show greater spin-orbit effect than in (OEP)ZrX_2L_2, which may be due to the smaller Ti out-of-plane distance. The data for Nb(V) and Ta(V) are similar to those of Zr(IV) and Hf(IV), respectively, but show greater spin-orbit coupling; they also show an unexplained wavelength dependence of luminescence. The Sc(III) porphyrins form binuclear μ-oxo complexes, which also show fluorescence and phosphorescence.

Over the past 6 years, d^0 transition-metal porphyrins containing Sc(III), Ti(IV), Zr(IV), Hf(IV), Nb(V), and Ta(V) have been synthesized and characterized.[4-9] In this paper, we collect the synthetic and chemical characterization work and present new spectroscopic studies of absorption and emission.[2] On the basis of these studies, we shall relate the electronic structure of these somewhat "exotic" metal complexes to previously studied metalloporphyrins. (For a recent review of "unusual metalloporphyrins", see ref 10.)

Metalloporphyrins fall into four distinct classes with regard to luminescence properties depending on the electronic structure of the metal.

(i) **Fluorescent** metalloporphyrins contain metal ions with closed shells, e.g., from groups 2A, 2B, 3A, and 4A.[11-15] They show both fluorescence and phosphorescence with systematic heavy-atom effects; i.e., fluorescence yield and phosphorescence lifetime generally decrease, and usually phosphorescence yield increases with increasing metal atomic number. Recent studies on group 4A metal complexes[15] show that counterion ligands such as Br^- and I^- have an even greater heavy-atom effect than the central metal ion itself. The heavy-atom effect is attributed to covalency of the empty porphyrin $e_g(\pi^*)$ orbital with orbitals on the metal and on the ligands.[15]

(ii) Phosphorescent metalloporphyrins contain metal ions with closed subshells, e.g., the d^6 metal ions Rh(III),[16] Ru(II),[17] and Pd(IV),[17] and the d^8 metal ions Pd(II) and Pt(II).[12,18] They show very strong phosphorescence with rather short phosphorescence lifetimes and extremely weak fluorescence.[16-19] These cases can be explained by far greater covalency between the empty porphyrin $e_g(\pi^*)$ orbitals and the filled d_π orbitals of the metal than in case i above.

(iii) Luminescent metalloporphyrins contain metal ions with unpaired electrons, e.g., d^9 Cu(II) and d^1 VO[12,20-23] or the recently discovered case of the d^3 metal ion Cr(III).[24,25] The excited states for one unpaired electron has been theoretically studied,[26] and it was shown that luminescence comes from both tripdoublet and quartet excited states. Because of the thermal equilibrium between these two spin states, the emission spectra and lifetimes show strong temperature dependence.[22]

(iv) Nonemitting metalloporphyrins are formed with a variety of transition metal ions. Since this negative characterization is rather hard to establish experimentally, we shall define this class operationally as having no clear luminescence that can be verified by excitation spectra. We have found no verifiable emission from metalloporphyrins containing Co(I), Co(II), Co(III), Ni(II) (see ref 18), Mo(V), W(V), Re(V) (see ref 27), Mn(III), and Ni(IV) (see ref 28). Porphyrins containing iron also show little or no luminescence. Such lack of luminescence may be a sign of low-energy charge transfer or d-d transitions lying between the normal phosphorescing porphyrin triplet state and the ground state.

Before we commenced these studies, we were unable to predict which of the four luminescence types would be found among the d^0 transition metal porphyrins. The studies reported here show that all of them fall into class i; they have substantial fluorescence and phosphorescence, with the relative strength of the two types of emission modified by the heavy-atom effect. Our results also show that the heavy-atom effect appears to be reduced as the metal moves out of the porphyrin plane.

The metalloporphyrins reported here have a number of structural types,[7] and it is useful to provide a general notational scheme. The parent porphines, octaethylporphine [(OEP)H_2] or α,β,γ,δ-tetraphenylporphine [(TPP)H_2], are indicated by numbers **1** or **2**, respectively. The metal porphines of the general formula (OEP)MX_n or (TPP)ScX (X denoting a normally univalent anionic axial ligand) have the coordination types A–F shown in Figure 1. No coordination type is yet assigned to (OEP)Nb(O)I_3 (**1G**) or (OEP)TaF_3 (**1H**), as their structural characterization is not yet complete. Moreover, in certain solvents, there appeared to be ligand exchange producing unknown coordination types, as discussed below.

Experimental Section

A. Synthesis. μ-Oxo-bis[(octaethylporphinato)scandium(III)] (1B or [(OEP)Sc]$_2$O). Anhydrous scandium trichloride (1 g) (the reaction will not work unless the material is anhydrous), octaethylporphyrin (1 g), and pyridine (20 ml, distilled from barium oxide) were sealed in a thick-walled glass tube. The mixture was heated at 200° for 18 hr, by which time the absorption spectrum (hand spectroscope) had changed from the four-lined metal-free to the two-lined metallocomplex. After cooling to room temperature, the contents of the tube was poured into water (50 ml). The aqueous mixture was extracted with methylene dichloride (10-ml aliquots) until all the porphyrin was in the organic layers. The combined organic layer was washed with water (5 × 50 ml), dried over sodium sulfate, filtered, and taken down to dryness under high vacuum (to remove the remaining pyridine). The purple residue was dissolved in a minimum of methylene dichloride and chromatographed on basic alumina (Woelm grade IV) using methylene dichloride as eluent. The metalloporphyrin, which on chromatography separates from some free base, was then taken down to dryness and redissolved in a minimum of methylene dichloride. This solution was boiled and the volume kept constant by the addition of cyclohexane. When crystals began to form, the mixture was allowed to stand at room temperature overnight. The product, as purple plates, was collected by filtration, washed with cold cyclohexane, and dried at room temperature. Yield was 872 mg, 79%. An analytical sample was recrystallized from methylene dichloride–cyclohexane.

Anal. Calcd for $C_{72}H_{88}N_8OSc_2$ (1170.6327 amu): C, 73.82; H, 7.57; N, 9.56. Found (M = 1170.6331 amu): C, 74.01; H, 7.52; N, 9.49.

An alternative method of preparation of **1B** is given in ref 5.

μ-Oxo-bis[(*meso*-tetraphenylporphinato)scandium(III)] (2B or [(TPP)Sc]$_2$O). The preparation was identical with the method described above for the octaethylporphyrin complex. One gram of $(TPP)H_2$ gave 921 mg (85%) of the product as glistening purple plates from methylene dichloride–cyclohexane. An analytical sample was recrystallized from methylene dichloride–cyclohexane.

Anal. Calcd for $C_{88}H_{56}N_8OSc_2$ (1330.3695 amu): C, 79.39; H, 4.24; N, 8.42. Found (M = 1330.3682 amu): C, 79.44; H, 4.17; N, 8.49.

(Octaethylporphinato)scandium Acetate [1C or (OEP)Sc(OAc)]. This compound was prepared according to the synthesis reported in ref 4.

(Octaethylporphinato)titanium Oxide [1D or (OEP)TiO] and (Octaethylporphinato)zirconium Diacetate [1E or (OEP)Zr(OAc)$_2$]. These compounds were prepared according to ref 4, 6, and 29.

(Octaethylporphinato)hafnium Diacetate [1F or (OEP)Hf(OAc)$_2$]. This compound was prepared from hafnium acetylacetonate obtained from metallic hafnium "Fluka" (Buchs, Switzerland) according to ref 4, 6, and 29 in a manner similar to the preparation of $(OEP)Zr(OAc)_2$.

(Octaethylporphinato)niobium Oxide Triiodide [1G or (OEP)Nb(O)I$_3$]. To 50 ml of boiling benzonitrile containing 500 mg (0.94 mmol) of $(OEP)H_2$ was added 1.5 g (5.5 mmol) of $NbCl_5$ (Fluka) and the mixture refluxed for 2 hr. A stream of dry nitrogen removed the HCl evolved during the reaction. After removal of the solvent in vacuo, the residue was dissolved in CH_2Cl_2 and chromatographed (silica; activity grade V). Traces of unreacted $(OEP)H_2$ were eluted with CH_2Cl_2. The main product followed with CH_2Cl_2/CH_3OH (7:3, v/v) and was crystallized from 9 ml of CH_2Cl_2/CH_3OH (4:5) containing 1 ml of aqueous ammonia (25%) as 406 mg (67%) of violet plates of $[(OEP)NbO]_2O$ [λ_{max} 572, 542, and 406 nm in benzene (log ϵ 4.22, 3.89, and 5.03); ir (KBr) 690, 742, and 785 cm^{-1}]. This product was dissolved in 4 ml of CH_2Cl_2-acetone (1:1), and then 0.5 ml of aqueous HI (67%) was added. The organic solvents were slowly evaporated. Washing with an aqueous KI solution (10%), water, a little methanol, and petroleum ether (40–60°) yielded 578 mg (89%) of dark violet plates of $(OEP)Nb(O)I_3$ (**1G**).

Anal. Calcd for $C_{36}H_{44}N_4OI_3Nb$ (1022.4 amu): C, 42.29; H, 4.34; N, 5.57; I, 37.29; Nb, 9.09. Found: C, 42.66; H, 3.46; N, 5.60; I, 37.79; Nb, 10.01.

Ir (KBr): 470, 353 cm^{-1}. Mass spectrum: A (mass number) = 641 [100%; $(OEP)NbO^+$], 625 [6%; $(OEP)Nb^+$], 254 [100%; I_2^+], 128 [100%; HI^+], 127 [100%; I^+]. A molecular ion for the similar compounds $(OEP)W(O)I_3$, $(OEP)Ta(O)I_3$, and $(OEP)W(O)I$ was likewise not observed.[29] **1G** was dried in vacuo at room room temperature. It liberated elemental iodine on heating in vacuo above 110°, indicating a degradation of the triiodide according to $(OEP)Nb(O)I_3 \rightarrow (OEP)Nb(O)I + I_2$. The same degradation was quantitatively examined in the tungsten series.[29]

(Octaethylporphinato)tantalum Trifluoride [1H or (OEP)TaF$_3$]. $(OEP)H_2$ [200 mg (0.37 mmol)], 400 mg (1.1 mmol) of $TaCl_5$ (Merck), and 500 mg of phenol were heated to 295° for 1 hr. Phenol was removed in vacuo at 100°. The residue was dissolved in CH_2Cl_2 and chromatographed on acid alumina (dry column; grade IV). After traces of $(OEP)H_2$, the main product was eluted with CH_2Cl_2 and gradually increasing amounts of CH_3OH (3 to 50%). After evaporation to dryness, the eluted material was dissolved in 12 ml of CH_2Cl_2/CH_3OH (1:5), and 2 ml of aqueous HF (20%) was added. The organic solvents escaped overnight, leaving 249 mg (86%) of violet needles of $(OEP)TaF_3$.

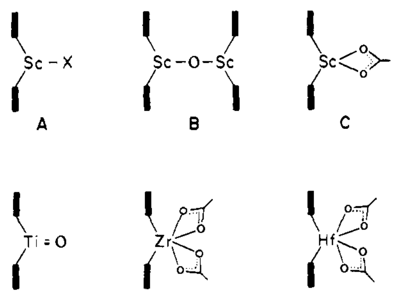

Figure 1. Coordination types for the d^0 metalloporphyrins: (OEP)ScX (1A), (TPP)ScX (2A), [(OEP)Sc]$_2$O (1B), [(TPP)Sc]$_2$O (2B), (OEP)ScOAc (1C), (OEP)TiO (1D), (OEP)Zr(OAc)$_2$ (1E), (OEP)Hf(OAc)$_2$ (1F).

Anal. Calcd for $C_{36}H_{44}N_4F_3Ta$ (770.7 amu): C, 56.10; H, 5.75; N, 7.27; F, 7.40; Ta, 23.48. Found: C, 58.28; H, 5.77; N, 6.91; F, 6.87; Ta, 23.27.

Mass spectrum: A = 770 [100%; $(OEP)^{181}TaF_3^+$], 751 [28%; $(OEP)TaF_2^+$], 732 [4%; $(OEP)TaF^+$]. Ir (KBr): 592 cm^{-1} (Ta–F).

The compound hydrolyzed in moist air liberating HF which etched the glass vessel in which the sample was contained. The products of this hydrolysis are unknown.

B. Spectroscopic Apparatus and Methods. All absorption spectra were taken on either the Cary 14 or 14H. The luminescence data were collected on the flexible system described briefly below and given in greater detail elsewhere.[15,16]

For simple emission and luminescence excitation data, a 1000-W tungsten-halogen source was used. Both the exciting and detecting beams were passed through Bausch and Lomb type monochromators with operating half-widths of 13.2 and 6.6 nm, respectively, for 2-mm slits. Signal detection and amplification were provided by a combination of an RCA 7265 photomultiplier tube (PMT) with a picoammeter or an RCA C-8852 PMT with a photon counter. The amplified signal was then recorded and/or fed into a PDP8/e computer for further data processing. All luminescence spectra were corrected for the wavelength sensitivity of the detectors, which were calibrated from the output of a standardized Eppley spectral irradiance lamp.

All quantum yields were measured relative to Zn etioporphyrin (ZnEtio), whose ϕ_f = 0.04 at both room temperature[30] and 77 K. The quantum yields were determined by the formula

$$\phi = \left(\frac{\text{Area}}{\Delta I\lambda_{\text{ex}}}\right)_{\text{sample}}\left(\frac{\Delta I\lambda_{\text{ex}}}{\text{Area}}\right)_{\text{ZnEtio}} \times 0.04$$

where Area is the integrated corrected luminescence spectrum; ΔI is the number of photons absorbed; and λ_{ex} is the exciting wavelength. All solutions studied were sufficiently dilute that reabsorption was negligible. This meant that $\Delta I/I$, the fraction of exciting light absorbed, was small. We originally used a Hewlett-Packard 833A radiant flux meter to measure ΔI as the difference between the intensity passing through the blank and that passing through the sample. However, we found that this was inaccurate because of instrument drift. For our final measurements, we used a photosensitive diode connected to a locally designed auto-null amplifier. This allowed us to offset for the current produced by the blank and to measure ΔI directly. However, as ΔI becomes small, slight differences in the optical paths of sample and blank introduce extraneous errors. This accounts for the range of values given for the quantum yields in some cases.

In all cases, except those that will be singled out in the subsequent text, we found that excitation spectra verified that the principal emission peak belonged to the principal absorbing species.

Table I. Absorption Peaks for d^0 Transition-Metal Porphyrins[a]

Compd	Solvent		N(0,0)	B(1,0)	B(0,0)	Q(2,0)	Q(1,0)	Q(0,0)	$\Delta_{1/2}$[d] (Q_{00})	$\Delta_{1/2}$[d] (B_{00})
(OEP)ScOAc	30/70[b]	λ	331	~385 sh	404	498	534	571	12	11.5
		A			23		1.00	1.62		
[(OEP)Sc]$_2$O	CCl_4	λ	332		394	~500	537	573[e]	17	21
		A			20		1.00	1.45		
(TPP)ScX[c]	CCl_4–MeOH	λ	350 sh	395	417	508	547	585	18	8
		A			28		1.00	0.08		
[(TPP)Sc]$_2$O	CCl_4	λ	345	~390	406	515	550	591	22	13
		A			24		1.00	0.165		
(OEP)TiO	CH_2Cl_2	λ	334	384	404	500	534	572		11
		ϵ	1.68	5.6	34.5	0.216	1.57	2.72		
(OEP)Zr(OAc)$_2$	CH_2Cl_2	λ	328	378	399	~490	528	565		7.5
		ϵ	1.58	6.6	38.0	0.224	1.20	3.16		
(OEP)Hf(OAc)$_2$	CH_2Cl_2	λ	328	378	398	~490	526	564		11
		ϵ	1.24	5.5	33.3	0.217	1.15	2.94		
(OEP)NbOI$_3$	$CHCl_3$	λ	342		406		535	569	28	35
		ϵ	2.28		8.8		0.67	1.37		
(OEP)TaF$_3$	$CHCl_3$	λ	375		401		527	565	17	13
		ϵ	4.25		23.9		1.0	3.08		

[a] Wavelength, λ, in nm; ϵ in M^{-1} cm^{-1} × 10^{-4}; A is absorbance. [b] 30% 1-butanol–70% 3-methylpentane. [c] Formed by [(TPP)Sc]$_2$O dissociation in solution. Axial ligand, X, unknown. [d] Band width in nm at half maximum. [e] Band has shoulder at ~577 nm. The absorbance A has been normalized for the Q(1,0) band.

Table II. Emission Peaks for d^0 Transition-Metal Porphyrins[a]

Compd	Solvent	λ_{ex}	Temp, °K	Q(0,0)	Q(0,1)	T(0,0)	T(0,1)
(OEP)ScOAc	30/70[b]		300	577	631		
			77	571	625	700	740
[(OEP)Sc]$_2$O	CCl_4		300	585	636		
			77	589	~639	714	
(TPP)ScX	30/70		300	598	644		
			77	598	643	746	~835
(OEP)TiO	CH_2Cl_2		300	577	632		
			77	582	640	712	
(OEP)TiO	30/70		300	576	631		
			77	583	641	714	762
(OEP)Zr(OAc)$_2$	CH_2Cl_2		300	569	622		
			77	565	618	703	
(OEP)ZrX$_2$L$_2$	30/70		300	576	631		
			77	570	622	704	746, 762
(OEP)Hf(OAc)$_2$	CH_2Cl_2		300	570	623		
			77	565	618	704	
(OEP)HfX$_2$L$_2$	30/70		300	577	629		
			77	568	620	704	745, 762
(OEP)NbOI$_3$	30/70	403[c]	300	580	635		
			77	575	629	718	
(OEP)TaF$_3$	30/70	390[d]	300	574	640		
			77	568	640	712	

[a] Wavelengths in nm. [b] 30% 1-butanol–70% isopentane. [c] Emission showed shoulder at 540 nm; another band appeared at 565 nm with λ_{ex} 525 nm. [d] Emission showed medium intensity band at 540 nm.

The excitation source for the lifetime measurements was a General Radio 1538 strobatac flash lamp with an externally controlled flash rate. Filters were used to isolate the exciting flash from the detector. After amplification, the PMT output was signal averaged by a PAR Model TDH-9 waveform eductor. The educted signals are logarithmic over two powers of ten.

C. Solvents. The solvents used for the absorption and room temperature emission spectra were reagent or spectroquality grade chlorinated methanes [CCl_4, $CHCl_3$, CH_2Cl_2] from Matheson Coleman and Bell (MCB), reagent grade methanol (MCB), and *n*-octane (Aldrich), which was dried with metallic Na before use. The solvents used for low-temperature quantum-yield measurements, because they freeze as transparent glasses, were chromatoquality 2-methyltetrahydrofuran (MCB), puriss. 3-methylpentane (Aldrich), and a 30%-70% mixture of reagent grade 1-butanol (MCB) with 3-methylpentane. The solvents were not further purified.

The solvents themselves or trace amounts of acid or water, even in seemingly inert solvents such as puriss. 3-methylpentane, were found to react with various of the metalloporphyrins. These phenomena will be discussed below.

Results

Parameters of the absorption spectra of the d^0 metalloporphyrins are given in Table I. Table II lists the emission maxima, and the luminescence yields and lifetimes are presented in Table III.

A. Sc Complexes (1A, 1B, 2A, 2B, and 1C). Although considerable spectroscopic work was carried out on solutions prepared from the binuclear μ-oxo species B, after analyzing the results, it became apparent that, in most cases, the μ-oxo compounds were largely or totally dissociated. They decomposed readily to mononuclear porphyrins A in puriss. 3-methylpentane and octane, as well as in alcohols. In addition, the Sc porphyrins were extremely sensitive to dissociation and demetallation in the presence of trace amounts of acid. The best solvent for preserving the μ-oxo species is very dry, acid-free CCl_4. (The behavior of the μ-oxo complex **1B** in solution is discussed in more detail in ref 5.)

Since much of the spectroscopic results for the mononuclear species A were obtained from solutions of dissociated

Table III. Luminescence Yields and Lifetimes for d^0 Transition-Metal Porphyrins

Compd	Solvent	λ_{ex}	ϕ_f(300 K)	ϕ_f(77 K)	ϕ_p(77 K)	ϕ_p/ϕ_f(77 K)	τ_p(77 K)[a]
(OEP)ScOAc	30/70[c]		0.14	0.16–0.21	0.046–0.056	0.29–0.26	400
[(OEP)Sc]$_2$O	CCl_4		s[e]	w	vw		
(TPP)ScX	30/70			0.08	0.003		
(OEP)TiO	3-MP[d]		0.02	0.06		0.05	175
(OEP)ZrX$_2$L$_2$	30/70		0.016	0.017	0.034	2.0	41
(OEP)HfX$_2$L$_2$	30/70		0.020	0.020	0.096	4.8	65
	30/70		0.007	0.007	0.171	24.4	8.4
(OEP)NbOI$_3$[b]	30/70	403	0.015				14.5
	2MeTHF	520	0.015				
	2MeTHF	525		0.027	0.074	2.7	
	2MeTHF	539		0.014	0.071	5.1	
	2MeTHF	558		0.016	0.17	10.5	
(OEP)TaF$_3$	30/70	390	~0.004	~0.004	0.47		2.5

[a] τ_p in msec. [b] Emission yields showed dependence on λ_{ex}. [c] 30% *n*-butane–70% 3-methylpentane. [d] 3-Methylpentane. [e] Symbols: s, strong; w, weak; vw, very weak. [The [(OEP)Sc]$_2$O is probably aggregated in CCl_4 at 77 K. See text.]

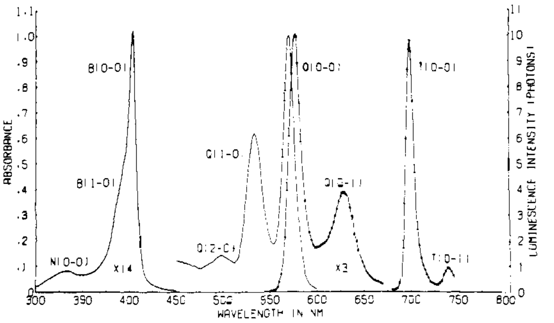

Figure 2. (OEP)ScX absorption spectrum (smooth line) at room temperature in CH_2Cl_2 and emission spectrum (stipled line) in a 30/70 mixture of 1-butanol and 3-methylpentane. The room-temperature fluorescence and 77 K phosphorescence are shown. The factors appearing under the bands in these spectra and in subsequent figures are the relative amounts by which these bands have been reduced.

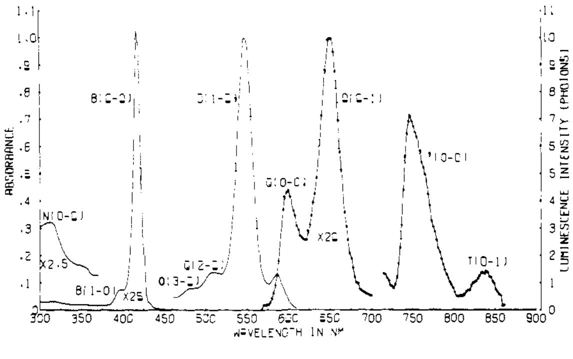

Figure 3. (TPP)ScX absorption spectrum (smooth line) in CCl_4-MeOH at room temperature and emission spectrum (stipled line) in 3-methylpentane. The room-temperature fluorescence and 77 K phosphorescence are shown.

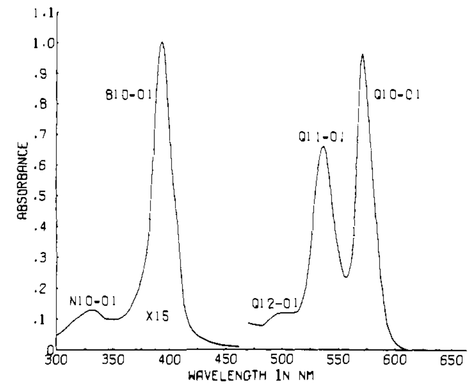

Figure 4. [(OEP)Sc]$_2$O room-temperature absorption spectrum in CCl_4.

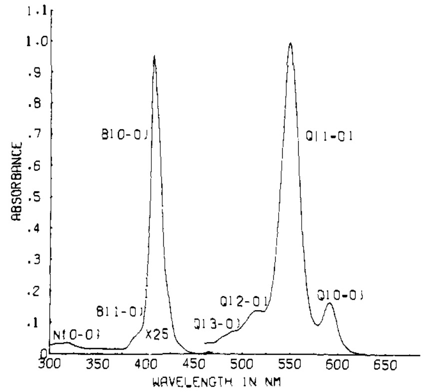

Figure 5. [(TPP)Sc]$_2$O room-temperature absorption spectrum in CCl_4.

binuclear species B, the identity of the axial ligand X is often uncertain. In 1-butanol, X is most probably OC_4H_9.[5] Furthermore, (OEP)ScOAc (**1C**) was found to undergo axial ligand exchange in methanol, but probably not in 1-butanol or 3-methylpentane. These axial ligand exchanges and uncertainties were evident from spectral shifts on the order of 2-3 nm. In the mononuclear OEP series, for instance, progressing from lower to higher wavelengths, we found (OEP)ScOAc in methanol < (OEP)ScOAc in 1-butanol or 3-methylpentane < (OEP)ScX from the dissociated [(OEP)Sc]$_2$O in 1-butanol or 3-methylpentane. In Tables I to III, we report data for (OEP)ScOAc in 30% 1-butanol–70% 3-methylpentane, because the acetate seems to be stable in that solvent. All (TPP)ScX was obtained from dissociated [(TPP)Sc]$_2$O.

The absorption spectra of (OEP)ScX and (TPP)ScX, shown in Figures 2 and 3, are rather similar to the corresponding Zn(d^{10}) complexes.[12] Their emission spectra show very strong fluorescence with moderate phosphorescence. The phosphorescence lifetime of (OEP)ScOAc of 0.4 sec is the longest yet measured for any porphyrin, and its fluorescence yield of 0.2 is also extremely high for a metalloporphyrin. The (TPP)ScX emission yields are lower and phosphoresence lifetimes shorter than those of the (OEP)ScX. This trend has been found in comparisons of other metal OEP and TPP complexes.[14] The apparent increase in the fluorescence yields at lower temperatures may be an oxygen effect[14] or an experimental artifact.

The absorption spectra of the binuclear μ-oxo complexes [(OEP)Sc]$_2$O and [(TPP)Sc]$_2$O (**1B** and **2B**) in CCl_4 are given in Figures 4 and 5 and in Table I. Two features are apparent in the comparison of the absorption spectra of the mononuclear A and the binuclear B. (i) The Soret band of B is shifted about 700 cm^{-1} to the blue of the Soret of A.

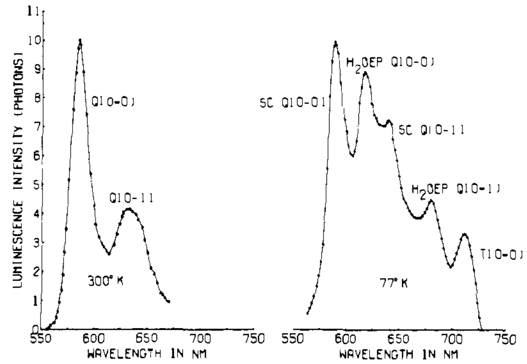

Figure 6. $[(OEP)Sc]_2O$ emission spectra at room temperature (left) and at 77 K (right) in CCl_4. At room temperature, the $(OEP)H_2$ impurity fluorescence is completely masked by the fluorescence of the μ-oxo dimer; both species show comparable fluorescence intensity at 77 K. This effect appears to be due to aggregation at low temperature. See text.

The Soret of B is also less intense and has a significantly broader half-width. (ii) The visible bands of B have a slight red shift relative to A. In the case of OEP, we find that **1B** has a broader Q(0,0) band than **1A**, and that the intensity ratio of O(0,0)/Q(1,0) is lower in **1B** than in **1A**. However for TPP, we find the intensity ratio of Q(0,0)/Q(1,0) is higher in **2B** than in **2A**. Earlier theoretical work allows interpretation of this opposite behavior of the intensity ratio.[31] It was shown that a red spectral shift among metallo derivatives of OEP correlates with a decrease of Q(0,0) while, among metallo derivatives of TPP, the red shift correlates with an increase of Q(0,0). The red shift, in turn, can be related to a shift of electron density from metal to ring.[31] Thus the spectral differences between A and B for both OEP and TPP can be explained if formation of the μ-oxo dimer causes a small shift of electron density onto the ring. Such a shift could also contribute to the upfield shift observed in the NMR of **1B** with respect to **1A**.[5]

Because the μ-oxo dimer dissociated in all of our glass-forming solvents, we were forced to study its emission in CCl_4, which forms a snow at 77 K. The results are shown in Figure 6. At room temperature, a very strong dimer emission is observed, but this is greatly reduced at 77 K. It can be seen in Figure 6 that emission from a small amount of $(OEP)H_2$ impurity, which is not apparent at 77 K, gives nearly half the observed low-temperature emission. Further studies now in progress have shown that strong dimer emission can be observed in very dry, highly purified 3-methylpentane glass at 77 K.[32] So the quenching shown in Figure 6 in CCl_4 at 77 K is probably due to aggregation.

B. Group 4B Complexes. (OEP)TiO (**1D**) is analogous in structure to the vanadylporphyrins,[33] whereas the metals in $(OEP)Zr(OAc)_2$ and $(OEP)Hf(OAc)_2$ (**1E** and **1F**) are eight coordinate with both acetates bidentate on the same side of the porphyrin ring,[5,29,34,35] as shown in Figure 1. These structural differences probably cause chemical and spectroscopic differences observed between the TiO and the Zr, Hf complexes.

(OEP)TiO dissolves readily in polar solvents and is quite stable in potentially reactive solvents such as alcohols or 2-methyltetrahydrofuran (2-MeTHF). The spectrum remains unchanged in 1-butanol.[24] $(OEP)Zr(OAc)_2$ and $(OEP)Hf(OAc)_2$ also dissolve readily in polar solvents, however, solutions in 1-butanol or 2-MeTHF exhibit spectral red shifts of 5 to 6 nm[24] which suggest that some type of ligand exchange has occurred. Most likely the original diacetates **1E** and **1F** are solvolyzed to yield another octacoordinate species $(OEP)ZrX_2L_2$ or $(OEP)HfX_2L_2$, where X = OAc or OC_4H_9 and L = C_4H_9OH. However, the exact coordination type of **1E** and **1F** after solvolysis in 30% 1-butanol and 70% 3-methylpentane is not known. The emission spectra of Figure 8 are of such species.

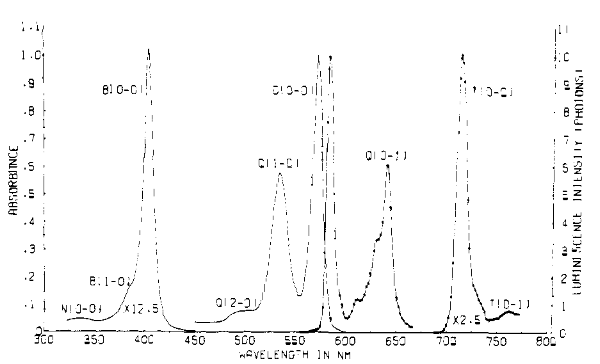

Figure 7. (OEP)TiO room-temperature absorption spectrum (solid line) in CH_2Cl_2 and 77 K emission spectrum (stipled line) in a 30/70 mixture of 1-butanol and 3-methylpentane.

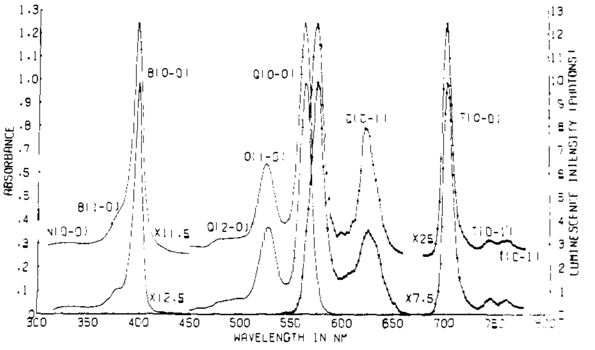

Figure 8. $(OEP)Zr(OAc)_2$ (lower) and $(OEP)Hf(OAc)_2$ (upper) room-temperature absorption spectra (smooth lines) in CH_2Cl_2 and emission spectra of their solvolysis products (stipled lines) in a 30/70 mixture of 1-butanol and 3-methylpentane. The room-temperature fluorescence and 77 K phosphorescence are shown.

A trace of $(OEP)H_2$ impurity could be detected in both the Zr and Hf compounds, but it was not severe enough to warrant further purification. The Hf sample was found to contain about 3-5% Zr impurity, which was revealed both in the mass spectrum and in the phosphorescence lifetime. This, however, is the standard impurity level quoted by various suppliers of Hf salts. Both Zr and Hf porphyrins demetallate in the presence of acid, but not as readily as the Sc porphyrins.

Figures 7 and 8 show the absorption spectra in CH_2Cl_2 and emission spectra in a 30%-70% mixture of 1-butanol and 3-methylpentane (30/70) of the (OEP)TiO and the Zr-Hf porphyrins, respectively. Figure 8 emphasizes the similarity of the spectra of the Zr and Hf prophyrins. The absorption spectra of the group 4B porphyrins are quite "normal" in that they exhibit the expected N, B, and Q bands.[11] The Soret or B(0,0) bands are sufficiently sharp that the B(1,0) bands are fairly well resolved. The absorption peaks in CH_2Cl_2 are given in Table I.

Although $(OEP)Zr(OAc)_2$ (**1E**) and $(OEP)Hf(OAc)_2$ (**1F**) may at first glance appear to have identical absorption spectra, there exist some small differences between the two. The spectrum of **1F** is slightly red shifted relative to **1E**, coupled with a slight decrease in the Q(0,0)/Q(1,0) band maxima ratio. **1F** has a broader, less intense Soret band. The spectrum of (OEP)TiO (**1D**) shows a considerable red shift relative to **1E** and **1F** in CH_2Cl_2 which is coupled again to an appreciable decrease in the Q(0,0)/Q(1,0) intensity ratio. The Soret band of (OEP)TiO is surprisingly broad and short. As mentioned above, for metal octaethyl-

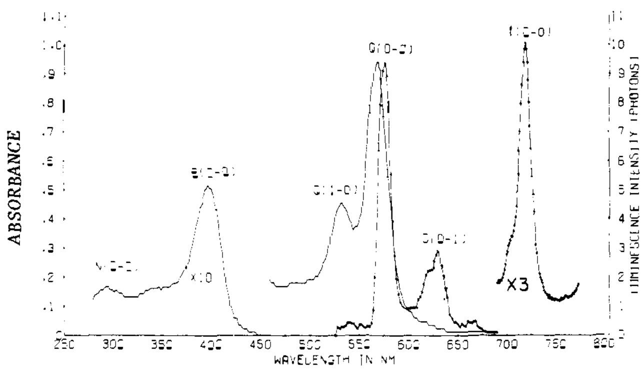

Figure 9. (OEP)Nb(O)I$_3$ room-temperature absorption spectrum (smooth line) and 77 K emission spectrum (stipled line) in a 30/70 mixture of 1-butanol and 3-methylpentane. λ_{ex} = 403 nm for the emission.

porphine, there is a correlation between red shift and weakened Q(0,0), which is attributed to a shift of electrons from metal to ring.[31]

The group 4B porphyrins exhibit moderate fluorescence and phosphorescence. Their emission spectra in both CH_2Cl_2 and 30/70 are listed in Table II where it can be seen that fluorescence of (OEP)TiO is virtually identical in either solvent, but the fluorescence of the Zr-Hf species is appreciably red shifted in 30/70. The absorption shifts of the Zr-Hf porphyrins in 30/70 parallel the fluorescence shifts.[24] The gap between Q(0,0) of absorption and Q(0,0) of emission is ~130 cm^{-1} for all species. The first excited singlet-state vibronic spacing of ~1250 cm^{-1} is substantially less than that of the ground state, ~1550 cm^{-1}. This is also true for the group 4A porphyrins[15] and has been explained by vibronic theory.[36] Two vibronic bands are observed for the phosphorescence of (OEP)ZrX$_2$ and for (OEP)HfX$_2$. These are labeled T(0,1′) and T(0,1) in Figure 8. Only one vibronic band was found for (OEP)TiO, but that may be due to the RCA 7265 photomultiplier tube insensitivity in this region. Another curious feature, perhaps due to the difference in coordination between (OEP)TiO and the Zr-Hf porphyrins, is that the fluorescence spectrum of (OEP)TiO red shifts at 77 K, whereas the Zr-Hf porphyrins show blue shifts (Table II). The luminescence yields and lifetimes are presented in Table III.

C. (OEP)Nb(O)I$_3$ and (OEP)TaF$_3$ (1G and 1H) proved to be very labile with respect to exchange of axial ligands. This was also evident from proton magnetic resonance spectra.[29] It resulted in our observing several luminescing species which could not be separated by column chromatography.[27] As a result we were unable to obtain samples with luminescence characteristic of a single molecular species so that the luminescence data are of qualitative value only.

The absorption spectra in CHCl$_3$ of 1G and 1H are given in Figures 9 and 11 and Table I. The absorption spectra are qualitatively similar to the other d^0 transition metal mononuclear OEP porphyrins. An interesting spectral feature is the broadening of all bands in the Nb species compared with the bands of the Ta species. The half-widths of all the bands of both compounds ($\Delta_{1/2}$ in Table I) demonstrate this phenomenon. The broadening of the Nb bands might explain the low Nb molar extinction coefficients, down a factor of 2 from Ta, since it is the peak integrated area that should be conserved between the two. The Nb spectrum is red shifted by ~5 nm relative to the Ta, coupled by an appreciable decrease in the Q(0,0)/Q(1,0) band maxima ratio.

The emission spectra of (OEP)Nb(O)I$_3$ in various solvents were fairly extensively studied. Because of possible ligand exchange, the exact composition of the luminescing species is not known. Figure 9 shows a fairly normal-looking fluorescence and phosphorescence emission at 77 K in 30% 1-butanol and 70% 3-methylpentane with Soret excitation. The excitation spectrum of Figure 10, again in 30/70 (uncorrected for the spectral output of the lamp), resembles the absorption of Figure 9 sufficiently that we are confident that the main absorbing species is the main emitting species. Unfortunately, with visible (Q band) excitation in either 30/70 or 2-methyltetrahydrofuran (2-MeTHF), the normal emission behavior of the niobylprophyrins is lost. Extra bands appear to the blue of the Q(0,0) fluorescence. In 2-MeTHF, different exciting wavelengths produce different phosphorescence quantum yields (Table III). Furthermore the 77 K phosphorescence excitation spectrum contains an intense 558-nm peak, which does not appear in either the absorption (Figure 9) nor the 30/70 fluorescence excitation (Figure 10) spectra. Apparently 30/70 and 2-MeTHF are reacting with the (OEP)Nb(O)I$_3$ and reacting in different ways. (2-MeTHF is known to deteriorate even the relatively stable zinc porphyrins.) Thus our fluorescence and phosphorescence yields are only of qualitative significance.

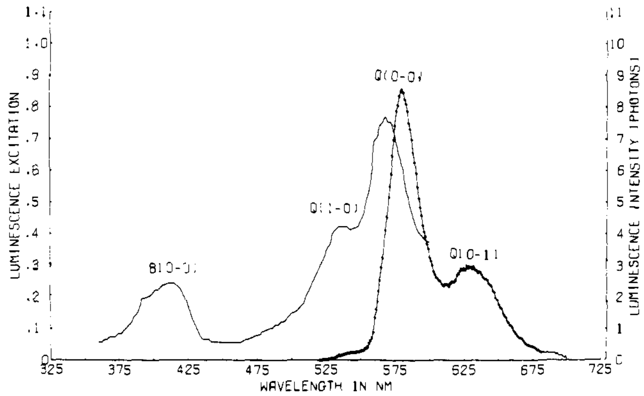

Figure 10. (OEP)Nb(O)I$_3$ room-temperature luminescence excitation (smooth line) and fluorescence (stipled line) spectra in a 30/70 mixture of 1-butanol and 3-methylpentane. The excitation spectrum is uncorrected for variations in lamp intensity. λ_{det} = 629 nm; λ_{ex} = 403 nm.

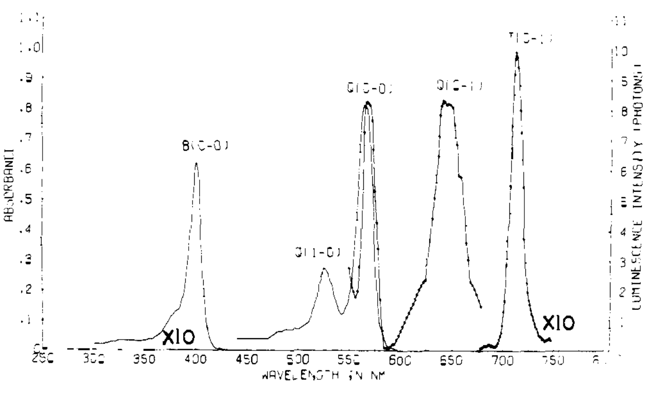

Figure 11. (OEP)TaF$_3$ room-temperature absorption spectrum (smooth line) and 77 K emission spectrum (stipled line) in a 30/70 mixture of 1-butanol and 3-methylpentane. λ_{ex} = 390 nm. The weak fluorescence of the compound is distorted by impurity fluorescence.

The absorption and luminescence of (OEP)TaF$_3$ are given in Figure 11. The excitation spectrum parallels the absorption. The sample contained some free base impurity, and perhaps another impurity, which account for the lack of mirror symmetry between absorption and fluorescence in Figure 11 and for inaccuracy in the low ϕ_f value reported in Table III. The compound seemed to show curious behavior similar to (OEP)Nb(O)I$_3$, but it was not as carefully studied, because impurity fluorescence obscured the weak (OEP)TaF_3 fluorescence.

In spite of all the irregularity of the fluorescence, the phosphorescence T(0,0) wavelength was invariant with regards to solvent and λ_{ex} for both the Nb and Ta species. Also for both species, the phosphorescence decay was exponential with one lifetime. Thus the lifetimes reported in Table III are correct.

Discussion

A. **Sc(III) complexes** (**1A** and **1C**) have fluorescence quantum yields quite similar to those of (OEP)$SiCl_2$,[15] which together seem to be the highest reported for porphyrins. [Related rings, e.g., chlorophyll, phthalocyanine, and tetrabenzoporphin, show higher values for ϕ_f,[14,30] presumably because of substantially shorter radiative lifetimes.] The similarity of ϕ_f for Sc(III) and Si(IV) porphyrins suggests that the radiationless rates $k(S_1 \rightsquigarrow T_1)$ are comparable in the two compounds. The phosphorescence yield ϕ_p of the (OEP)ScX is more than twice that of (OEP)$SiCl_2$, and its lifetime is roughly four times longer. For metalloporphyrins the quantum yield for the process $S_1 \rightsquigarrow S_0$ is generally low.[13,14] If this be true for (OEP)$SiCl_2$ and (OEP)ScX, then the radiationless rate $k(T_1 \rightsquigarrow S_0)$ and the radiative rate $k(T_1 \rightarrow S_0)$ are, respectively, four times and two times faster in the Si than in the Sc complex.

How can this very low spin-orbit coupling in (OEP)ScX be explained? Spin-orbit effects in porphyrins are attributed to covalency of the empty porphyrin $e_g(\pi^*)$ orbitals with the metal d_π or ligand p_x, p_y orbitals.[15] The spin-orbit effect in (OEP)$SiCl_2$ may have a strong contribution from the Cl ligands, while the nonplanarity of the Sc(III) metal may reduce overlap of d_π and $e_g(\pi^*)$ as discussed below. The combination of the two effects may produce a lower spin-orbit effect in (OEP)ScX than in (OEP)$SiCl_2$. The triplet lifetime of 400 msec for (OEP)ScX is also longer than 115 msec reported for an etioporphyrin aluminum(III) complex.[13] Again the greater nonplanarity of Sc(III) as compared with Al(III) porphyrin is probably the cause of lower spin-orbit effect observed in the heavier metal.

We were for some time inclined to accept at face value the quenching of the μ-oxo dimer fluorescence observed in CCl_4 at 77 K.[24] The appearance of the strong free-base fluorescence, shown in Figure 6, encouraged us in this view. More recent studies show that $[(OEP)Sc]_2O$ gives strong fluorescence and phosphorescence in 3-methylpentane at 77 K.[32] If, as now seems likely, aggregation is responsible for the quenching of the dimer emission shown in Figure 6, it could be that the free base impurity is acting as a trap with respect to excitation of the metalloporphyrin. [We have recently observed impurity trap emission in films of octaethylporphine.[37]] Studies are currently in progress on the low-temperature dimer emission that hopefully will determine dimer quantum yield and the effect of CCl_4.[32]

B. **Group 4B Complexes.** A comparison of (OEP)ZrX_2L_2 and (OEP)HfX_2L_2 shows a clear heavy-atom effect; ϕ_f decreases, ϕ_p increases, and τ_p decreases for the heavier metal. However, when ϕ_f, ϕ_p, τ_p of (OEP)TiO and (OEP)ZrX_2L_2 are compared, the lighter metal shows a greater "heavy atom" effect. To explain this anomalous behavior, comparison with other metalloporphyrins is useful. On comparison to group 4A,[15] we find that (OEP)ZrX_2L_2 qualitatively falls between (OEP)$GeCl_2$ and (OEP)$SnCl_2$, whereas (OEP)HfX_2L_2 qualitatively falls between (OEP)$SnCl_2$ and (OEP)$PbCl_2$. (This match does not hold exactly for all measurables ϕ_f, ϕ_p, and τ_p.) Thus, if we attribute spin-orbit coupling to mixing between $e_g(\pi^*)$ and d_π,[15] we must conclude that this mixing is about the same for the group 4B atoms Zr and Hf as for the group 4A atoms Ge, Sn, and Pb. Yet the atomic configuration in group 4B is s^2d^2 while, in group 4A, it is s^2p^2. Thus we would expect greater d_π covalency in group 4B complexes than in group 4A (all other factors being equal). This expected behavior is shown by (OEP)TiO, which shows greater spin-orbit effect than (OEP)$GeCl_2$. (OEP)TiO shows substantially greater spin-orbit effect than (OEP)ScX, although the two compounds have similar absorption spectra and have essentially the same atomic number.

We explain these various comparisons by proposing that the spin-orbit coupling in Sc(III), Zr(IV), and Hf(IV) porphyrins is substantially reduced by the large displacement of the metal from the porphyrin plane. Although X-ray data for a Sc porphyrin complex are not available, recent X-ray crystallographic results show that Ti is 0.58 Å out-of-plane in ($OEPMe_2$)TiO,[38] whereas Zr is >1.0 Å out-of-plane in (OEP)$Zr(OAc)_2$.[35] [Although the identity and geometry of the luminescing species (OEP)ZrX_2L_2 is unknown, it is probably safe to presume that the basic eight-coordinate geometry is maintained.] As the metal is displaced from the porphyrin plane, $e_g(\pi^*)$ overlap with d_π will be reduced. This in turn reduces covalency and hence reduces the metal contribution to spin-orbit coupling. A second, probably less important factor, may be the degree of covalency of $e_g(\pi^*)$ with the p_x, p_y orbitals of oxygen. This effect would be larger in (OEP)TiO than in (OEP)ScX since O is double bonded to Ti [Ti=O bond is 1.62 Å in ($OEPMe_2$)TiO],[38] while X is only singly bound to Sc. There should be very little effect of ligands on spin-orbit coupling for (OEP)ZrX_2L_2 or (OEP)HfX_2L_2. Finally we note that the absorption spectra indicate an increased donation of electrons from the metal to the ring in (OEP)TiO. This effect may also relate to the smaller out-of-plane displacement of the TiO moiety and the length of the Ti=O double bond.

C. **Group 5B complexes, (OEP)Nb(O)I_3 and (OEP)TaF_3,** proved labile in solution so that the reported quantum yields have only qualitative significance. However, the yield and lifetime data clearly show that spin-orbit coupling is greater in Nb(V) than in Zr(IV), and greater in Ta(V) than in Hf(IV) complexes. The group 5B metals are expected to have greater metal d_π covalency with the porphyrin $e_g(\pi^*)$, because the group 5B d_π orbitals should have lower energy than the group 4B d_π orbitals. Furthermore, within the species actually present in the solutions examined, the Nb or Ta ion may be closer to the porphyrin plane than in the Zr and Hf species discussed above.

Conclusion

All d^0 metal porphyrins are *fluorescent*, i.e., show significant fluorescence and phosphorescence as modified by the heavy-atom effect. Minor variations within this general category arise because of the local geometry around the central metal; in particular, metal nonplanarity appears to reduce the heavy-atom effect.

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Chemistry of Dicarbonyl η^5-Cyclopentadienyliron Complexes. General Syntheses of Monosubstituted η^2-Olefin Complexes and of 1-Substituted η^1-Allyl Complexes. Conformational Effects on the Course of Deprotonation of (η^2-Olefin) Cations

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Abstract: Reaction of dicarbonyl η^5-cyclopentadienyl(η^1-allyl)iron with cationic electrophiles provides a general route to monosubstituted (η^2-olefin)iron complexes. Alternatively these may be obtained by an exchange reaction employing the olefin and dicarbonyl η^5-cyclopentadienyl(η^2-isobutylene)iron tetrafluoroborate. Deprotonation of the cationic olefin complexes provides a general route to 1-substituted η^1-allyliron complexes. The most stable conformation for the monosubstituted (η^2-olefin)iron cation is best represented by **17b**. The stereochemistry of the η^1-allyliron complexes derived by deprotonation of the complex cations can be accounted for in terms of preferred base abstraction of an allylic proton trans to the iron-olefin bond. Deprotonation of the allyl alcohol complex (**3p**) leads to the lactone (**26**) through a conformationally determined stereospecific intramolecular reaction. The ^{13}C NMR spectra of several (η^2-olefin)iron cations are recorded and shown to provide useful information relevant to their conformations. Deuteration of dicarbonyl η^5-cyclopentadienyl(η^1-cinnamyl)iron with deuteriotrifluoroacetic acid is shown to be nonstereospecific.

In order to examine the synthetic applications of $(3 + n)$ cycloaddition reactions[1] and of metal-assisted olefin condensations[2] employing dicarbonyl η^5-cyclopentadienyl-(η^1-allyl)iron complexes [hereafter designated as (η^1-allyl)Fp complexes], general methods for the preparation of these substances are required. Simple alkyl-substituted (η^1-allyl)Fp complexes have been prepared by metallation of the corresponding allyl halides or tosylates with the dicarbonyl η^5-cyclopentadienyl ferrate anion (Fp^-)[3] or through deprotonation of the dicarbonyl η^5-cyclopentadienyl(olefin)iron cation [Fp(olefin)$^+$].[1b] These latter complexes are in turn available either directly from the olefin by an exchange reaction with the Fp(isobutylene) cation[4] or through a reaction sequence involving the complex iron anion (Fp^-) and an epoxide.[5] These transformations are summarized below in Figure 1.

The present paper provides a general procedure for the introduction of functional groups at the terminal olefinic carbon atom of (η^1-allyl)Fp complexes, and a description of the chemistry of the intermediate Fp(olefin) cations, in particular their conformation and the stereochemistry of their deprotonation.

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