Porphyrians. XXXI.¹ Chemical Properties and Electronic Spectra of d⁰ Transition-Metal Complexes²

Martin Gouterman,*³a Louise Karle Hanson,³a Gamal-Eddin Khalil,³a Johann W. Buchler,³a Klaus Rohbok,³b and David Dolphin³c

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98195, the Institut für Anorganische Chemie, Technische Hochschule, D-51 Aachen, West Germany, and the Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1W5.

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Abstract: The octaethylporphin complexes of forms (OEP)MX₄L₄, (OEP)MO, and (OEP)M(OM)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 (φₑ ≈ 0.2) and phosphorescence lifetimes (τₛ ≈ 400 msec) of (OEP)ScX show very low spin–orbit coupling, i.e., no heavy-atom effect. The complexes of (OEP)ZrX₂L₂ and (OEP)HfX₄L₂ have fluorescence yields (φₑ ≈ 0.02 and 0.007), phosphorescence yields (φₛ ≈ 0.096 and 0.171), and phosphorescence lifetimes (τₛ = 65 and 8.4 msec) that exhibit regular heavy-atom effects; the values for (OEP)TiO₂ 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, d⁰ transition-metal porphyrins containing Sc(III), Ti(IV), Zr(IV), Hf(IV), Nb(V), and Ta(V) have been synthesized and characterized. In this paper, we collect the synthetic and chemical characterization work and present new spectroscopic studies of absorption and emission. 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 complexes¹⁵ 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 e₂(π*) orbital with orbitals on the metal and on the ligands.¹⁵

(ii) Phosphorescent metalloporphyrins contain metal ions with closed subshells, e.g., the dⁱ metal ions Rh(III),¹⁶ Ru(II),¹⁷ and Pd(IV),¹⁷ and the d⁶ metal ions Pt(II) and Pt(IV).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 e₂(π*) orbitals and the filled dₗ orbitals of the metal than in case i above.

(iii) Luminescent metalloporphyrins contain metal ions with unpaired electrons, e.g., d⁵ Cu(II) and d⁴ VO²⁺⁻²⁻ or the recently discovered case of the d⁴ metal ion Cr(III).¹²,²³ The excited states for one unpaired electron have been theoretically studied,²⁶ and it was shown that luminescence comes from both triplet doublet and quartet excited states. Because of the thermal equilibriums 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 d⁰ 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,²⁻² and it is useful to provide a general notational scheme. The parent porphyrines, octaethylporphine [(OEP)H₂] or a,b,γ,δ-tetraphenylporphine [(TPP)H₂], are indicated by numbers 1 or 2, respectively. The metal porphyrines of the general formula (OEP)MX₄, 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)I₃ (1G) or (OEP)TaF₃ (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(octaethylporphinate)scandium(III) (1B) or (OEPSc)₂O. 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 spec-
troscosc had changed from the four-lined metal-free to the two-lined metallocomplex. After cooling to room temperature, the contents of the tube were poured into water (50 ml). The aqueous mixture was extracted with methylen chloride (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.

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

µ-Oxobis(meso-tetraphenylporphino)scandium(III) (2B or [TTP]ScO). The preparation was identical with the method described above for the octaethylporphin complex. One gram of (TTP)H2 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 C39H34N4O8: C, 58.91; H, 4.74; N, 7.27; F, 5.57; I, 10.01. Found: C, 58.22; H, 4.77; N, 7.26; F, 5.52; I, 10.00.

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

(Octaethylporphino)titanium oxide [1D or (OEP)TiO] and (Octaethylporphino)zirconium Acetate [1E or (OEP)Zr(OAc)2]. These compounds were prepared according to refs 4, 6, and 29.

(Octaethylporphino)hafnium Diacetate [1F or (OEP)Hf(OAc)2]. This compound was prepared from hafnium acetylacetonate obtained from metallic hafnium (Buchs, Switzerland) according to ref 4, 6, and 29 in a manner similar to the preparation of (OEP)Hf(OAc)2.

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 photomultiplier tube. 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 φ0 = 0.04 at both room temperature30 and 77 K. The quantum yields were determined by the formula

\[ \phi = \left( \frac{\text{Area}}{\Delta \lambda_{\text{ex}} \times 0.04} \right) \times \frac{\Delta \lambda_{\text{em}}}{\text{Area}_{\text{ZnEtio}}} \]

where Area is the integrated corrected luminescence spectrum; Δλ is the number of photons absorbed; and λmax is the exciting wavelength. All solutions studied were sufficiently dilute that reabsorption was negligible. This meant that Δλ/λ, the fraction of exciting light absorbed, was small. We originally used a Hewlett-Packard 833A radiant flux meter to measure Δλ 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 Δλ directly. However, as Δλ 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.

Figure 1. Coordination types for the d0 metalloporphyrins: (OEP)ScX (1A), (TPP)ScX (2A), (OEP)ScO (1B), (TPP)ScO (2B), (OEP)ScOAc (1C), (OEP)TiO (1D), (OEP)Zr(OAc)2 (1E), (OEP)Hf(OAc)2 (1F).
are logarithmic over two powers of ten.

The solvents used for low-temperature quantum-yield measurements, because they freeze as transparent glasses, were chromato-

quality 2-methyltetrahydrofuran (Aldrich), which was dried with metallic Na before use.

The excitation source for the lifetime measurements was a PAR Radio 1538 strobatac flash lamp with an externally controlled flash rate. Filters were used to isolate the exciting flash from the general Radio 1538 strobatac flash lamp with an externally controlled flash rate. Filters were used to isolate the exciting flash from the parallel emission spectra were reagent or spectroquality grade [MCB] (Aldrich), and a 30%-70% mixture of reagent grade 1-butanol with isopentane. 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 d⁰ 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 in solution. Axial ligand, X, unknown.

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

<table>
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<tr>
<th>Compd</th>
<th>Solvent</th>
<th>λ (nm)</th>
<th>B(0.0)</th>
<th>Q(1.0)</th>
<th>Q(0.0)</th>
<th>Δι/Δσ</th>
<th>η/σ</th>
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<td>(OEP)ScOAc</td>
<td>30/70</td>
<td>332</td>
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<td>1.00</td>
<td>1.62</td>
<td>11.5</td>
<td>12</td>
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<tr>
<td>[OEP]Sc₂O</td>
<td>CCl₄</td>
<td>332</td>
<td>0.00</td>
<td>1.00</td>
<td>1.45</td>
<td>21</td>
<td>17</td>
</tr>
<tr>
<td>(TPP)ScX</td>
<td>MeOH</td>
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<td>0.00</td>
<td>1.00</td>
<td>0.08</td>
<td>8</td>
<td>18</td>
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<tr>
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<td>CCl₄</td>
<td>345</td>
<td>0.00</td>
<td>1.00</td>
<td>0.165</td>
<td>11</td>
<td>22</td>
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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 parallel emission spectra were reagent or spectroquality grade [MCB] (Aldrich), and a 30%-70% mixture of reagent grade 1-butanol with isopentane. 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.

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Table I. Absorption Peaks for d⁰ Transition-Metal Porphyrins

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<thead>
<tr>
<th>Compd</th>
<th>Solvent</th>
<th>N(0,0)</th>
<th>B(0.0)</th>
<th>Q(2,0)</th>
<th>Q(1,0)</th>
<th>Q(0,0)</th>
<th>Δι/Δσ</th>
<th>η/σ</th>
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<tr>
<td>(OEP)ScOAc</td>
<td>30/70</td>
<td>331</td>
<td>~385</td>
<td>404</td>
<td>498</td>
<td>534</td>
<td>571</td>
<td>12</td>
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<tr>
<td>[OEP]Sc₂O</td>
<td>CCl₄</td>
<td>332</td>
<td>394</td>
<td>~500</td>
<td>537</td>
<td>573e</td>
<td>17</td>
<td>21</td>
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<tr>
<td>(TPP)ScX</td>
<td>MeOH</td>
<td>350</td>
<td>395</td>
<td>417</td>
<td>508</td>
<td>547</td>
<td>585</td>
<td>18</td>
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<tr>
<td>[TPP]Sc₂O</td>
<td>CCl₄</td>
<td>345</td>
<td>~390</td>
<td>406</td>
<td>515</td>
<td>550</td>
<td>591</td>
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Table II. Emission Peaks for d⁰ Transition-Metal Porphyrins

<table>
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<tr>
<th>Compd</th>
<th>Solvent</th>
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<th>Temp, °K</th>
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<th>Q(0,1)</th>
<th>T(0,0)</th>
<th>T(0,1)</th>
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<td>300</td>
<td>577</td>
<td>631</td>
<td>700</td>
<td>740</td>
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<td>746</td>
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<td>598</td>
<td>643</td>
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<td>332</td>
<td>300</td>
<td>598</td>
<td>643</td>
<td>714</td>
<td>762</td>
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<td>(OEP)ZrOAc₂</td>
<td>CH₂Cl₂</td>
<td>332</td>
<td>300</td>
<td>598</td>
<td>643</td>
<td>714</td>
<td>762</td>
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<tr>
<td>(OEP)ZrX₄</td>
<td>MeOH</td>
<td>350</td>
<td>300</td>
<td>576</td>
<td>631</td>
<td>703</td>
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<tr>
<td>(OEP)HfOAc₂</td>
<td>CH₂Cl₂</td>
<td>332</td>
<td>300</td>
<td>570</td>
<td>622</td>
<td>704</td>
<td>746, 762</td>
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<tr>
<td>(OEP)HfX₄</td>
<td>MeOH</td>
<td>350</td>
<td>300</td>
<td>576</td>
<td>618</td>
<td>704</td>
<td>704</td>
</tr>
<tr>
<td>(OEP)TaF₄</td>
<td>403e</td>
<td>300</td>
<td>577</td>
<td>620</td>
<td>704</td>
<td>745, 762</td>
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a Wavelength, λₑₓ in nm; b 30% 1-butanol–70% 3-methylpentane. c Formed by [(TPP)Sc]₂O 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.

C. Solvents. The solvents used for the absorption and room temperature emission spectra were reagent or spectroquality grade chlorinated methanes [CCl₄, CH₂Cl₂, CH₃Cl₂] 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 chromatography 2-methyltetrahydrofuran (MCB), purified 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.
order of 2-3
and uncertainties were evident from spectral shifts on the
stance, progressing from lower to higher wavelengths, we
found
butanol or 3-methylpentane. These axial ligand exchanges
Furthermore, (OEP)ScOAc
Figure 2. (OEP)ScX absorption spectrum (smooth line) at room temperature in CH2Cl2 and emission spectrum (stippled 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 CCl4-MeOH at room temperature and emission spectrum (stippled line) in 3-methylpentane. The room-temperature fluorescence and 77 K phosphorescence are shown.

binuclear species B, the identity of the axial ligand X is often uncertain. In 1-butanol, X is most probably OC4H9.5
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]2O 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]2O.

The absorption spectra of (OEP)ScX and (TPP)ScX, shown in Figures 2 and 3, are rather similar to the corre-

Table III. Luminescence Yields and Lifetimes for d8 Transition-Metal Porphyrins

<table>
<thead>
<tr>
<th>Compd</th>
<th>Solvent</th>
<th>λex (nm)</th>
<th>ϒ(300 K)</th>
<th>ϒ(77 K)</th>
<th>ϒp(77 K)</th>
<th>ϒp/ϒ(77 K)</th>
<th>τp(77 K) [a]</th>
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<tbody>
<tr>
<td>(OEP)ScOAc</td>
<td>30/70</td>
<td>304</td>
<td>0.14</td>
<td>0.16-0.21</td>
<td>0.046-0.056</td>
<td>0.29-0.26</td>
<td>400</td>
</tr>
<tr>
<td>[(OEP)Sc]2O</td>
<td>CCl4</td>
<td>304</td>
<td>w</td>
<td>w</td>
<td>w</td>
<td>w</td>
<td>w</td>
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<tr>
<td>(TPP)ScX</td>
<td>30/70</td>
<td>304</td>
<td>0.08</td>
<td>0.08</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>(OEP)FIO</td>
<td>3-MPd</td>
<td>304</td>
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<td>0.06</td>
<td>0.05</td>
<td>0.05</td>
<td>175</td>
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<tr>
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<td>0.017</td>
<td>0.034</td>
<td>2.0</td>
<td>4.1</td>
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<tr>
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<td>0.020</td>
<td>0.020</td>
<td>0.096</td>
<td>4.8</td>
<td>65</td>
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<tr>
<td>(OEP)TaX3L4</td>
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<td>0.007</td>
<td>0.171</td>
<td>24.4</td>
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<td>(OEP)NbX3L4</td>
<td>30/70</td>
<td>0.016</td>
<td>0.016</td>
<td>0.17</td>
<td>10.5</td>
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<tr>
<td>(OEP)TaF3</td>
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<td>390</td>
<td>-0.004</td>
<td>-0.004</td>
<td>0.47</td>
<td>0.47</td>
<td>2.5</td>
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</table>

[a] τp in msec. [b] Emission yields showed dependence on λex. [c] 30% n-butane-70% 3-methylpentane. [d] 3-Methylpentane. [e] Symbols: s, strong; w, weak; vw, very weak. [The [(OEP)Sc]2O is probably aggregated in CCl4 at 77 K. See text.]

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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. 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. 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 CC14, 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)H2 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 CC14 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 nm24 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)ZrX2L2 or (OEP)HfX2L2, where X = OAc or OCH3 and L = CH3OH. However, the exact coordination type of 1E and 1F after solvolysis is 30% 1-butanol and 70% 3-methylpentane is not known. The emission spectra of Figure 8 are of such species.

A trace of (OEP)H2 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 CH2Cl2 and emission spectra in a 30%–70% mixture of 1-butanol and 3-methylpentane. The room-temperature fluorescence and 77 K phosphorescence are shown.

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 CH2Cl2 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-
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.\textsuperscript{31}

The group 4B porphyrins exhibit moderate fluorescence and phosphorescence. Their emission spectra in both CH$_2$Cl$_2$ 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.\textsuperscript{24} The gap between Q(0,0) of absorption and Q(0,0) of emission is $\sim$130 cm$^{-1}$ for all species. The first excited singlet-state vibronic spacing of $\sim$1250 cm$^{-1}$ is substantially less than that of the ground state, $\sim$1550 cm$^{-1}$. This is also true for the group 4A porphyrins\textsuperscript{15} and has been explained by vibronic theory.\textsuperscript{36} Two vibronic bands are observed for the phosphorescence of (OEP)ZrX$_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.

The absorption spectra in CH$_2$Cl$_2$ 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 macroheme 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 is corrected for variations in lamp intensity. $\lambda_{em} = 659$ nm, $\lambda_{ex} = 403$ nm.

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

Figure 10. (OEP)Nb(O)h$_3$ room-temperature luminescence excitation spectrum (smooth line) and fluorescence (stippled line) spectra in a 30/70 mixture of 1-butanol and 3-methylpentane. The excitation spectrum is uncorrected for variations in lamp intensity. $\lambda_{em} = 659$ nm, $\lambda_{ex} = 403$ nm.

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

The absorption and luminescence of (OEP)TaF$_3$ 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 absorption. The absorption 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 niobylporphyrins 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)h$_3$ 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.

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 $\phi_r$ value reported in Table III. The compound seemed to show curious behavior similar to (OEP)Nb(O)h$_3$, but it was not as carefully stud-
ied, because impurity fluorescence obscured the weak (OEP)TaF₃ fluorescence.

In spite of all the irregularity of the fluorescence, the phosphorescence T(0,0) wavelength was invariant with regard to solvent and T₀ₑₓ 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)SiCl₂,¹⁵ which together seem to be the highest reported for porphyrins. [Related rings, e.g., chlorophyll, phthalocyanine, and tetrazenzoporphyrazine, show higher values for φₚ.¹⁴,¹⁵ Presumably because of substantially shorter radiative lifetimes.] The similarity of φₚ for Sc(III) and Si(IV) porphyrins suggests that the radiationless rates k ∈ S₁ → T₁ are comparable in the two compounds. The phosphorescence yield φₚ of the (OEP)ScCl₂ is more than twice that of (OEP)SiCl₂, and its lifetime is roughly four times longer. For metalloporphyrins the quantum yield for the process S₁ → S₀ is generally low.¹³,¹⁴ If this be true for (OEP)SiCl₂ and (OEP)ScCl₂, then the radiationless rate k ∈ T₁ → S₀ and the radiative rate k ∈ (T₁ → S₀ 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 eg(π*) orbitals with the metal dₚ or ligand pₓ, pᵧ orbitals.¹⁵ The spin–orbit effect in (OEP)SiCl₂ may have a strong contribution from the Cl ligands, while the nonplanarity of the Sc(III) metal may reduce overlap of dₓ and eg(π*) as discussed below. The combination of the two effects may produce a lower spin–orbit effect in (OEP)ScX than in (OEP)SiCl₂. The triplet lifetime of 400 msec for (OEP)SiCl₂ 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 CCl₄ at 77 K.³⁴ 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.³⁵ If, as now seems likely, aggregation is responsible for the quenching of the dimer emission shown in Figure 6, it would be true 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 octaethylporphyrin ³⁷] Studies are currently in progress on the low-temperature dimer emission that hopefully will determine dimer quantum yield and the effect of CCl₄.³²

B. Group 4B Complexes. A comparison of (OEP)ZrX₂L₂ and (OEP)HₓZrX₂L₂ shows a clear heavy-atom effect; φₚ decreases, φₓ increases, and Tₓ decreases for the heavier metal. However, when φₓ, φₓ, φₓ, and Tₓ of (OEP)TiO and (OEP)ZrX₂L₂ 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)ZrX₂L₂ qualitatively falls between (OEP)GeCl₂ and (OEP)SnCl₂, whereas (OEP)HₓZrX₂L₂ qualitatively falls between (OEP)SnCl₂ and (OEP)PbCl₂. (This match does not hold exactly for all measurable φₓ, φₓ, and Tₓ.) Thus, if we attribute spin–orbit coupling to mixing between eg(π*) and dₓ,¹² 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 s²d² while, in group 4A, it is s²p². Thus we would expect greater dₓ 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)GeCl₂. (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 (OEPMe₂)TiO,³⁸ whereas Zr is >1.0 Å out-of-plane in (OEP)Zr(OAc)₆.³⁵ Although the identity and geometry of the luminescing species (OEP)ZrX₂L₂ 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, eg(π*) overlap with dₓ 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 eg(π*) with the pₓ, pᵧ 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 (OEPMe₂)TiO],³⁸ while X is only singly bound to Sc. There should be very little effect of ligands on spin–orbit coupling for (OEP)ZrX₂L₂ or (OEP)HₓZrX₂L₂. 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 T₁=O double bond.

C. Group 5B complexes, (OEP)Nb(OI)₃ and (OEP)TaF₃, 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 dₓ covalency with the porphyrin eg(π*), because the group 5B dₓ orbitals should have lower energy than the group 4B dₓ 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 d⁴ 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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References and Notes


(3) (a) University of Washington; (b) Technische Hochschule Aachen; (c) University of British Columbia.


(17) A. Antipas, M. Gouterman, D. B. Howell, J. W. Buchler, and D. Dolphin, work in progress.


(34) J. van Kaam, Diplomarbeit, Technische Hochschule Aachen, 1972.

(35) N. Kim, J. W. Buchler, and J. L. Hoard, to be published.

