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Tetraphenylporphyrin Molecules Containing Heteroatoms Other Than Nitrogen. 7.[1] Emission and Electronic Structure of Rings Containing Sulfur and Selenium

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We report on S and Se substituted tetraphenylporphyrins, where S and/or Se replace the central NH groups. S_2TPP shows fluorescence with $\lambda_{max} = 705$ nm, lifetime 1.3 ns, and quantum yield $\phi_f = 0.01$. No phosphorescence is observed at 77 K in a solvent with 20% ethyl iodide. The acid dication of S_2TPP also fluoresces with $\lambda_{max} = 766$ nm, lifetime 0.49 ns, and quantum yield $\phi_f = 0.11$. However, SSeTPP and Se_2TPP show no emission nor do their acid dications. Iterative extended Hückel (IEH) calculations predict an allowed charge-transfer (CT) transition $Se(\sigma^*) \rightarrow \pi^*$ at much lower energy than the analogous $S(\sigma^*) \rightarrow \pi^*$. The lack of fluorescence is attributed to this transition occurring at lower energy than the $\pi \rightarrow \pi^*$. Curve fitting of the lowest energy optical absorption bands in H_2TPP, S_2TPP, SSeTPP, and Se_2TPP reveals that the Se-containing compounds have an extra band in the long-wavelength tail with $\lambda_{max} = 715$ nm (Se_2TPP) and 705 nm (SSeTPP) that we attribute to the charge-transfer transition. Analysis of the IEH bond orders shows that contracted outer-valence d orbitals must be included to explain the cross-ring bonding, which increases in the order S–S < S–Se < Se–Se. The calculations raise the possibility that, while S_2TPP^+ is a π radical, Se_2TPP^+ may be either a π or a $Se(\sigma^*)$ radical.

Introduction

The three molecules of interest in this study are the group 6 substituted tetraphenylporphyrins obtained by setting A = B = S (S_2TPP), A = B = Se (Se_2TPP), and A = S, B = Se (SSeTPP) in Figure 1. For comparison, known properties of free-base tetraphenylporphyrin, A = B = NH (H_2TPP), are also reported. The syntheses and optical absorption spectra of the chalcogen porphyrins have been published,[3] and studies of high-resolution ^1H NMR have been reported.[1a] The chalcogen porphyrins have normal free-base absorption spectra: meaning that they have the usual intense near-UV band (Soret) and the four-banded (Q_{I-IV}) visible spectrum. Such normal spectra are adequately explained by the four-orbital model.[4]

In this paper we present studies on the emission spectra of the chalcogen porphyrins. These data are interpreted by theoretical studies based on the iterative extended Hückel (IEH) model. The theoretical studies are also used to interpret the optical absorption spectra, ^1H NMR, and X-ray structural data on the compounds as well as ESR and optical data on the radical cations and anions.

When we began these studies, there were several questions that deserved attention: (1) Is there bonding between the group 6 atoms across the core of the porphyrin? (2) Do the outer-valence d orbitals of the group 6 atoms participate in the electronic structure ? (3) Are low-energy charge-transfer (CT) states predicted? (4) Is much spin–orbit coupling predicted?

The first two questions have their roots in ref 1a, where it is suggested that through hybridization of the p_z, d_{yz}, and d_{xz} atomic orbitals on the group 6 atoms, significant bonding can occur across the core of the porphyrin. The bonding explains the abnormally short X-ray distances observed[5] (S–S = 3.05 Å, S–Se = 2.89 Å, Se–Se = 2.85 Å), at the same time maintaining the observed C–X–C (where X = S or Se) angle of ~90°, as well as the observation that the nuclear least-squares plane (NLSP) of S_2TPP is more "puckered" than the NLSP of Se_2TPP. (See Table I.) Notice that the observed distances are markedly shorter than the sum of the van der Waals radii (S–S = 3.70 Å, S–Se = 3.85 Å, Se–Se = 4.00 Å)[6] and have the reverse trend.

Table I. Deviation from the Porphyrin Ring Plane[a]

atom[b]	dist from NLSP, Å[c]		atom[b]	dist from NLSP, Å[c]	
	S_2TPP	Se_2TPP		S_2TPP	Se_2TPP
S or Se	−0.142	−0.103	C_4	0.066	0.058
N	0.199	0.013	C_5	0.049	0.004
C_{12}	−0.135	−0.052	C_6	−0.167	0.007
C_1	0.008	−0.014	C_7	−0.150	0.034
C_2	0.118	0.047	C_8	0.072	0.010
C_3	0.031	−0.003	C_9	0.051	0.001

[a] Based on X-ray data from ref 5. [b] See Figure 1 for numbering scheme. [c] NLSP is the nuclear least-squares plane formed by the porphine-like subunit, i.e., ignoring phenyls.

The question of group 6 d-orbital participation in bonding has received much attention.[7] Schomaker and Pauling[8] tacitly suggest such a participation in thiophene to explain many of its properties. Later Longuet-Higgins[9] invoked pd hybridization of the sulfur atomic orbitals in a molecular orbital treatment of thiophene. Maeda[7f] recognized the need for contracted Slater type d orbitals if effective pd hybridization is to occur. There have been many arguments given that support contracted d orbitals under certain bonding conditions.[7a–e,10] As we shall show here, inclusion of contracted d orbitals is required if the IEH calculations are to explain the X-ray data on the chalcogen porphyrins.

Question 3 naturally arises when quasi-aromatic compounds containing heteroatoms with nonbonding electrons are studied,

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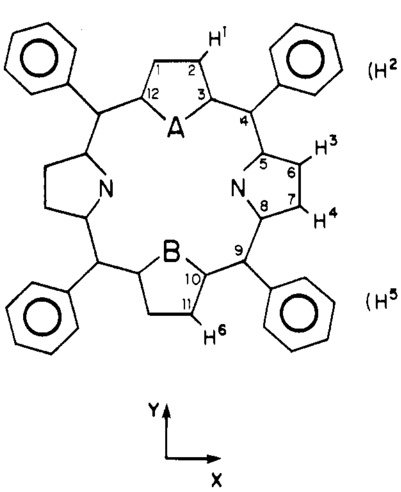

Figure 1. Geometry and numbering scheme for the porphyrins in this study: A = B = NH (H_2TPP); A = B = S (S_2TPP); A = B = Se (Se_2TPP); A = S, B = Se (SSeTPP). The phenyls are replaced by H atoms (H^2 and H^5) in the calculations.

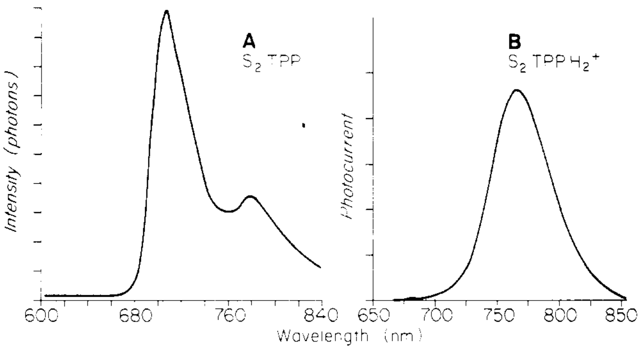

Figure 2. (A) Room-temperature emission spectrum of S_2TPP in benzene; λ_{exc} = 515 nm. (B) Room-temperature emission of S_2TPP in benzene with two drops of TFA; λ_{exc} = 465 nm. Note that (B) is uncorrected for the wavelength sensitivity of the detector.

and question 4 arises when a study is made of a series of molecules such as H_2TPP, S_2TPP, SSeTPP, and Se_2TPP, where there is a serial increase in heavy atoms. Our studies show that charge-transfer transitions occur at low energy in the Se compounds; however, we were unable to obtain information on spin–orbit coupling.

Emission Studies

A. S_2TPP. The room-temperature emission spectrum of S_2TPP in benzene is shown in Figure 2A. The relative emission intensity has been corrected for photomultiplier tube and emission monochromator response as a function of wavelength. The apparatus used is a noncommercial instrument previously described.[12a] Maximum wavelengths of emission occur at 705 and 777 nm. The uncorrected excitation spectrum taken on a Perkin-Elmer MPF-44A fluorescence spectrophotometer coincided very well with the absorption spectrum of S_2TPP in benzene.

The observed fluorescence lifetime (τ_{measd}) of the emission from the S_2TPP solution is 1.30 ns, compared to τ_{measd} = 9.5 ns for the emission from a H_2TPP solution measured on the same instrument (see Table II for τ_{measd}). The lifetime apparatus consists of a cavity-dumped tunable dye laser, synchronously pumped by a mode-locked argon ion laser, with time-correlated single-photon counting.[12b]

Table II. Lifetimes and Quantum Yields[a]

molecule	τ_1, ns	τ_2, ns	τ_{measd}, ns	ϕ_f'	$\phi_{f,1}$	$\phi_{f,2}$
H_2TPP	93		9.5 ± 0.5			
S_2TPP	130	180	1.30 ± 0.05	0.0097	0.0100	0.0072
SSeTPP	120			$<10^{-5}$		
Se_2TPP	110			$<10^{-5}$		
$S_2TPPH_2^{2+}$	4.4		0.49 ± 0.03		0.11	

[a] τ_1 and τ_2 are natural radiative lifetimes from eq 3 and 4. τ_{measd} is experimental. ϕ_f' and $\phi_{f,i}$ are quantum yields from eq 1 and 2.

The fluorescence quantum yield, ϕ_f, of S_2TPP was estimated by two independent methods:

$$\phi_f' = \{[F(S_2TPP)][A(H_2TPP)]/[F(H_2TPP)] \times [A(S_2TPP)]\}[\phi_f(H_2TPP)] \quad (1)$$

$$\phi_{f,i} = \tau_{measd}/\tau_i^{nat} \quad (2)$$

Equation 1 gives the quantum yield of S_2TPP relative to H_2TPP. Here F(molecule) is the integrated fluorescence emission and A(molecule) is the absorbance. We excite both molecules at the same wavelength. $\phi_f(H_2TPP)$ is taken as 0.11.[13] The details on determining F are given elsewhere.[11] Equation 2 is the ratio of the observed emission lifetime, τ_{measd}, to the natural radiative lifetime, τ^{nat}. We calculated two τ^{nat} values

$$\tau_1^{-1} = 2.88 \times 10^{-9} n^2 (g_l/g_u) \langle \nu^2 \rangle \int \epsilon(\nu)\, d\nu \quad (3)$$

which is an equation derived for atoms[14] that is often applied to molecules with immeasurable fluorescence, and

$$\tau_2^{-1} = 2.88 \times 10^{-9} n^2 (g_l/g_u) \langle \nu_f^{-3} \rangle^{-1} \int [\epsilon(\nu)] \nu^{-1}\, d\nu \quad (4)$$

which is an equation derived for molecules.[15] In equation 3 and 4 ν refers to wavenumber.[16] The integrals were evaluated by Simpson's rule.[11] The index of refraction for benzene makes n^2 = 2.25 over the wavelength range of interest.

Values of ϕ_f', ϕ_f, τ_2, and τ_1 are listed in Table II. τ_1 for H_2TPP was calculated as a reference. The τ_1 = 93 ns is in good agreement with the reported value of 99 ns.[13] τ_2 and τ_1 for S_2TPP are very similar, lending credence to τ_1 for Se_2TPP and SSeTPP. The percent differences between ϕ_f' and $\phi_{f,i}$ are within expected experimental error.

No additional bands were observed in the 77 K emission spectrum of S_2TPP dissolved in an ether–isopentane–ethyl iodide (2:2:1) solvent. This places the upper limit of phosphorescence yield at 10^{-3}. It should be noted that the phosphorescence yield of H_2TPP has been reported as $\phi_p \approx 2 \times 10^{-5}$.[17]

B. S_2TPP Conjugate Acid. The conjugate acid of S_2TPP is formed by placing two drops of trifluoroacetic acid (TFA) in a benzene solution of S_2TPP.[3b] The uncorrected emission spectrum of the conjugate acid (Figure 2B) shows a maximum at 766 nm. The lack of any vibronic bands may be due to the long-wavelength falloff in the spectral response of the Perkin-Elmer 650-10S fluorescence spectrophotometer. The uncorrected excitation spectrum indicated that the emission was from the main absorber. The measured radiative lifetime and the quantum yield determined from τ_1^{nat} are given in Table II.

C. SSeTPP and Se_2TPP. Both of these compounds in benzene showed weak emission at 705 nm. However, examination of the excitation spectra revealed that S_2TPP was the emitting species. This impurity was most likely introduced

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Table III. IEH Parameters for Sulfur and Selenium

atom	STO	ζ	1st VSIP, eV[d]	2nd VSIP, eV[d]
S	3s[a]	2.034	21.286	32.966
S	3p[a]	1.700	11.615	22.310
S	3d[b]	1.200	3.199	8.650
Se	4s[a]	2.400	20.137	32.009
Se	4p[a]	1.950	10.575	21.192
Se	4d[c]	1.330	2.719	9.020

[a] ζ values from ref 22. [b] ζ value from ref 7a. [c] ζ value calculated from eq 9 in ref 11. [d] The VSIP approximation methods are described in ref 11.

Table IV. Bond Orders and d-Orbital Populations[a]

molecule	atoms k, l	$BO_{k,l}$[b]	τ $BO_{k,l}$[b]	N(d)[c]
S_2P	S, S	0.122 (−0.046)	0.022 (0.007)	0.192
SSeP	S, Se	0.182 (−0.078)	0.041 (0.010)	0.307
Se_2P	Se, Se	0.320 (−0.121)	0.061 (0.017)	0.382
S_2P	S, C_3		0.375 (0.351)	
	C_1, C_2		0.741 (0.726)	
	C_2, C_3		0.419 (0.440)	
	C_3, C_4		0.543 (0.551)	
	C_4, C_5		0.525 (0.528)	
	N, C_5		0.504 (0.514)	
Se_2P	Se, C_3		0.368 (0.348)	
	C_1, C_2		0.740 (0.726)	
	C_2, C_3		0.420 (0.442)	
	C_3, C_4		0.547 (0.554)	
	C_4, C_5		0.531 (0.534)	
	N, C_5		0.507 (0.518)	
H_2P[d]	HN, C_3		0.364[d]	
	C_1, C_2		0.769	
	C_2, C_3		0.524	
	C_3, C_4		0.631	
	C_4, C_5		0.588	
	C_5, N		0.599	
S_2	S, S	0.847 (0.492)		
Se_2	Se, Se	0.798 (0.498)		
SSe	S, Se	0.723 (0.352)		

[a] Bond orders (BO) involving S and Se atoms were calculated with use of eq 6. All others were calculated with use of eq 7. [b] Bond orders with d orbitals (in parentheses, without d orbitals). [c] d-Orbital populations. [d] From ref 36.

by some H_2S impurity present in the H_2Se reagent used in the initial synthesis.[3] The observed emission was used to estimate the molar ratio of S_2TPP impurity to SSeTPP as 3:100 and the amount of S_2TPP impurity to Se_2TPP as 8:1000.[11] Only the impurity emitted when Se_2TPP and SSeTPP were dissolved in ether–isopentane–ethyl iodide (2:2:1) at 77 K. Only the conjugate acid of the S_2TPP impurity emitted when Se_2TPP and SSeTPP were dissolved in a benzene–TFA mixture.

Table II shows that τ_1 for Se_2TPP, SSeTPP, and S_2TPP are all approximately equal. Therefore the lack of emission from the selenium-containing compounds must be due to greatly enhanced radiationless decay from the lowest excited singlet. Two mechanisms would seem possible: (1) The selenium compounds have a greatly enhanced intersystem crossing from $S_1 \rightsquigarrow T_1$; however, the enhancement must be such that the phosphorescence of T_1 is not observed due to fast radiationless decay $T_1 \rightsquigarrow S_0$. (2) There exists a mechanism to enhance the radiationless rate $S_1 \rightsquigarrow S_0$. Previous studies on porphyrin systems show that such an enhancement is most likely induced by the presence of a charge-transfer state between $S_1(\pi,\pi^*)$ and S_0.[18] It will be shown in the next sections that this latter mechanism is likely.

Electronic Structure

A. Method and Parameters. Our theoretical study of the electronic structure is based on the iterative extended Hückel (IEH) model, which has found broad qualitative applications in porphyrin electronic structure analysis.[18-21] We followed Zerner[19a] in the choice of interaction parameter $K = 1.89$ and in the orbital exponents and valence-state ionization potentials (VSIP) for C, H, and N atoms.

The IEH parameters used for sulfur and selenium are listed in Table III. The s and p orbital exponents for S and Se are from Cusachs.[22] The choice of exponent for the d orbital is not so obvious. Corrington[23] gives exponents for virtual Slater type orbitals (STO) for a large number of the main-group elements. But those orbitals proved much too diffuse.[11] Instead we used $\zeta_{3d} = 1.20$ for sulfur and $\zeta_{4d} = 1.33$ for selenium, which represent contracted d orbitals. A lengthy discussion of this choice is given elsewhere.[11] The valence-state ionization potentials (VSIP) were determined from the atomic energy levels given by Moore[24] with use of the decoupling scheme described by Zerner.[25] Details are given elsewhere.[11] Since the S and Se atoms had positive charge, the VSIP values for the anion were not needed.

For the reduction of computation time, calculations were done on the planar projected X-ray coordinates,[5] with replacement of the phenyls with H atoms. Thus the calculations were done on S_2P and Se_2P, assumed to have D_{2h} symmetry, and SSeP, assumed to be C_{2v}. The C–H distances were set at 1.08 Å.

B. IEH Bond Orders and Observed S–S, S–Se, and Se–Se Distances. The questions on the bonding between the central group 6 atoms and the role of d orbitals in that bonding are answered by a bond-order analysis. The LCAO–MO covalent bond order between two atoms k and l ($BO_{k,l}$) is derived by Cohen[26]

$$BO_{k,l} = \sum_{r,s} BO_{r_k s_l} = \sum_{r,s} (p_{r_k s_l} S_{r_k s_l} + p_{r_k s_l} f_{r_k s_l} g_{r_k s_l}) \qquad (5)$$

where $BO_{r_k s_l}$ = the bond order between orbital r on center k and orbital s on center l. (See Cohen[26] for definition of terms in eq 5.) Equation 5 was shown by Cohen to reduce to the Mulliken bond order[27] where there is one basis function per center and the centers are separated by typical covalent bond lengths. Therefore, the π bond orders ($\pi BO_{k,l}$) between the atomic pairs C_1–C_2, C_2–C_3, C_3–C_4, C_4–C_5, and N–C_5 were calculated with use of the Mulliken bond order

$$\pi BO_{k,l} = p_{r_k s_l}(1 + S_{r_k s_l}) \qquad (6)$$

where r and s are p_z atomic orbitals. The total bond order ($BO_{k,l}$) for the atomic pairs S–S, S–Se, and Se–Se, as well as the π bond orders for the pairs S–C_3 and Se–C_3 (when d orbitals are included), must be calculated with use of eq 5 because there is more than one function per center and the group 6 atoms are separated by distances greater than their normal covalent bond lengths. The needed reference overlap

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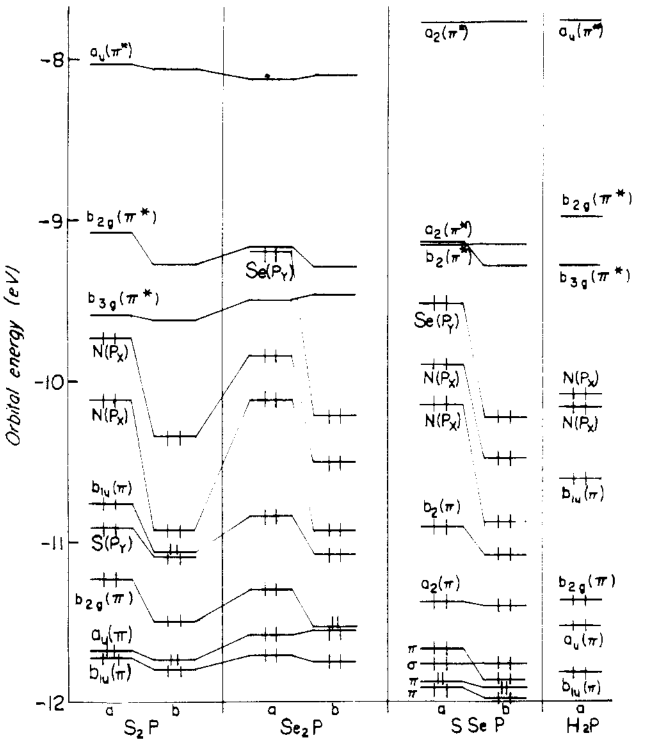

Figure 3. Iterative extended Hückel MO energy level diagram for S_2P, SSeP, and Se_2P. Energy levels of H_2P are from ref 19c: (a) calculations without d orbitals; (b) calculations with d orbitals. The compounds have D_{2h} symmetry labels except for SSeP, which is C_{2v}.

integrals[26] ($S_{r_k s_l}{}^R$) were calculated for the group 6 elements on the basis of a separation equal to the sum of the covalent radii for the two atoms involved.

The bond orders between the opposite group 6 atoms are given in Table IV. Also included in Table IV, for comparison, are the bond orders for the three diatomics: S_2, SSe, and Se_2. When the d orbitals *are not* included in the basis, the bond orders (numbers in parentheses) between the group 6 atoms in the chalcogen porphyrins are all negative, decreasing in the order S–S > S–Se > Se–Se. Such bond orders contradict the structural data quoted in the Introduction[1a,5] and analyzed in Table I. However, when d orbitals *are* included in the basis, the bond orders are all positive and increase in the order S–S < S–Se < Se–Se, which is in accord with the X-ray data.

The relative importance of the d orbitals in the chalcogen porphyrins can also be deduced with a Mulliken[27] population analysis to determine *N*(d), the fractional number of electrons in the d orbitals. These numbers, also given in Table IV, increase in the order S_2P < SSeP < Se_2P.

If the charge densities of the three molecules are compared for calculations with and without d orbitals, the charge densities on the S or Se atom change by less than 0.005 e. Therefore the d-orbital population can be thought of as "coming from" the s and p orbitals of the group 6 atom. This supports the proposal[1] that the X-ray structures require d-orbital hybridization.

C. IEH Charge-Transfer (CT) Transistions and the Observed Far-Red Absorption Bands. Figure 3 shows the molecular orbital (MO) energy levels provided by the IEH calculation; for comparison the levels of H_2P are included.[19c] Theoretical and spectroscopic studies have shown that the low-energy excited states of porphyrin arise from the four-orbital transitions $a_1(\pi),b_{1u}(\pi) \rightarrow b_{3g}(\pi^*),b_{2g}(\pi^*)$, in D_{2h} labels.[18] The calculation on H_2P shows two nitrogen nonbonding orbitals and a $b_{2g}(\sigma)$ orbital among the HOMO's. Their high energy is considered an artifact of the model, and transitions from these orbitals to the vacant π^* orbitals occur at highe energy than that implied by the figure.[18]

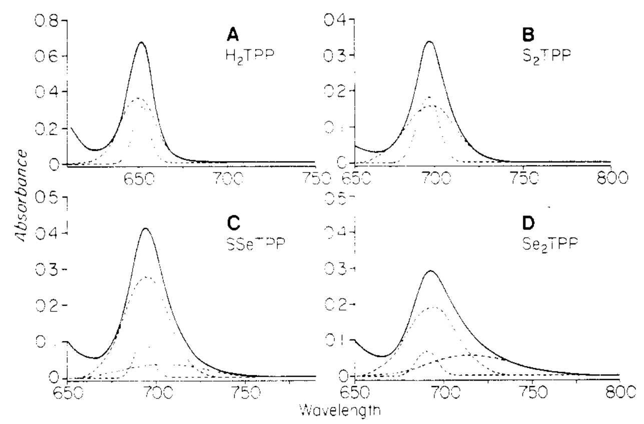

Figure 4. Curve fitting of the far-red absorption band in benzene: (A) H_2TPP; (B) S_2TPP; (C) SSeTPP; (D) Se_2TPP. The solid curve is both the absorption curve and the fitted curve. The broken curves are the individual Gaussians needed for a good fit.

The chalcogen porphyrins show another HOMO orbital, the antibonding X(p_y), X = S or Se. It can be seen that the energy of this orbital rises in the order S_2P < SSeP ≤ Se_2P, where the equals sign holds when d orbitals are included. Although the IEH model can be in error on charge-transfer (CT) transitions by 1–2 eV, relative shifts are reliable. Thus the calculations suggest that an allowed *z*-polarized CT transition, $b_{2u}(\sigma^*) \rightarrow b_{3g}(\pi^*)$, should occur in S_2TPP and Se_2TPP; it is $a_1(\sigma^*) \rightarrow b_2(\pi^*)$ in SSeTPP, the σ^* orbital is predominantly X(p_y) in origin, and the CT transition should be at lower energy in Se_2TPP and SSeTPP than in S_2TPP.

The IEH model does not allow prediction of the exact energy of these CT bands. The near-IR region was scanned for absorption bands, but none were found. However, analysis of the red end of the visible absorption spectrum reveals a far-red band in Se_2TPP and SSeTPP that is absent in H_2TPP and S_2TPP. The red absorption bands are shown in Figure 4. The absorption curves (solid lines), measured with a Varian Superscan 3, were fit with standard Gaussians (dashed curves) generated by a Du Pont Model 310 curve resolver. In each case the sum of the dashed curves equals the solid curve. The H_2TPP curve is non-Gaussian and requires the near superposition of two Gaussians (centered at 651 nm) for a good fit (Figure 4A). The same situation holds for S_2TPP (Figure 4B). However, SSeTPP and Se_2TPP require an additional broad band at 705 and 715 nm, respectively (Figure 4C,D), that we attribute to the *z*-polarized CT transition.

Now a few comments about the effects of d-orbital inclusion on the MO energies. Some orbitals rise in energy while others drop, depending on the change in the occupations of the atomic orbitals involved in the MO's. In the previous section it was noted that bonding occurs between the group 6 atoms when d orbitals are included in the basis. This fact is reflected in the lowering of the $b_{2u}(\sigma^*)$ MO when d orbitals are included. However, the σ^* MO is not stabilized enough to preclude a low-energy CT state in the Se-containing molecules.

It is of some value to discuss the quenching nature of the proposed charge-transfer state. The CT state is formed by removing an electron from a σ^* MO that is antibonding with respect to the Se–Se or S–Se interaction. Therefore, the Se atoms are expected to move closer together in the CT state and farther apart on relaxation to the ground state (S_0). This causes a large shape change in the molecule during the relaxation CT → S_0, which allows for a large Franck–Condon overlap between the lowest vibrational level of the CT state and the high-energy vibrational levels of S_0. This makes the radiationless decay rate from the CT state much faster than the radiationless decay from the $S_1(\pi,\pi^*)$ state where the shape of the molecule is not significantly different from the shape in the ground state. The enhanced radiationless decay rate would then account for the quenched emission. This interpretation is consistent with the broadness of the Gaussian required to fit the CT band.

D. IEH Comparisons to the Observed Properties of the Radical Cations and Anions. Optical and ESR studies have been carried out on the radical anions and cations of the chalcogen porphyrins by Fajer and Richardson at Brookhaven National Laboratory.[28] These studies show that the radical cations S_2TPP^+ and Se_2TPP^+ have substantially different optical spectra, while the spectra of the radical anions S_2TPP^- and Se_2TPP^- are very similar. As a result we carefully considered the possibility that Se_2TPP^+ is a Se(σ^*) radical while S_2TPP^+ is a ring π radical. Both species would be expected to have radical anions with the odd electron in $b_{3g}(\pi^*)$.

The hypothesis that the radical cations of Se_2TPP and SSeTPP are of different electronic nature from that of S_2TPP might be expected to affect the redox potentials, giving a smaller potential difference between the first oxidation and first reduction wave. These differences are 2.12, 2.08, and 2.02 V for S_2TPP, SSeTPP, and Se_2TPP, respectively.[1b] While the trend supports the hypothesis, these differences are too small to be significant.

The ESR results in the radical cations are as follows: $g(S_2TPP^+ = 2.0026$; $g(Se_2TPP^+) = 2.013$; a_S = unresolved; $a_{Se} = 15$ G; $2a_N(S_2TPP^+) = 2.3$ G; $2a_N(Se_2TPP^+) = 2.0$ G.[28] It should be noted that the g values for the anions shift similarly: $g = 2.0028$ for S_2TPP^- and $g = 2.0118$ for Se_2TPP^-.[28] SCF-MO PPP calculations on the radical cations by Richardson and Fajer predict similar unpaired spin densities for the two radicals.[28] They conclude that S_2TPP^+ and Se_2TPP^+ are both $b_{1u}(\pi)$ cation radicals and attribute the difference in g values to differences in spin-orbit coupling.

While the similarity in nitrogen hyperfine coupling for S_2TPP^+ and Se_2TPP^+ does support the view that both species are $b_{1u}(\pi)$ radicals, this datum does not settle the issue. The nitrogen 2s orbital is not included in the singly occupied MO for either $b_{1u}(\pi)$ or b_{2u}[Se(σ^*)] orbitals, so that to a first approximation $a_N = 0$ for both states. Thus the hyperfine splitting depends on configuration interaction.[29-32] The sizes of the exchange integrals are discussed elsewhere, and the conclusion is reached that a similar value of a_N for the π and the Se(σ^*) radical would not be too surprising.[11]

In another approach to the issue we examined $\int \epsilon \, d(\ln \lambda)$ for the S_2TPP^+ and Se_2TPP^+ radicals. It can be shown that the total dipole strength for the four orbital transitions [$a_{1u}(\pi), a_{2u}(\pi) \rightarrow e_g(\pi^*)$ in D_{4h}] in the π cation radical is only three-fourths that of the neutral. This results from the fact that the two top filled π orbitals have only three electrons. The argument would not apply to a Se(σ^*) radical. Although the four-orbital model is not adequate for radicals due to the presence of other transitions,[33] the qualitative intensity prediction might be expected to be useful in the present context. We evaluated $\int \epsilon \, d(\ln \lambda)$ for S_2TPP^+, S_2TPP, Se_2TPP^+, and Se_2TPP from 305 to 995 nm. The experimental integrals stand in the ratio 1:1.14:1.04:1.03. The near equality of the integrals for S_2TPP^+ and Se_2TPP^+ argues for a π cation; however, the near equality of the integrals for Se_2TPP^+ and Se_2TPP argues for a Se(σ^*) radical.

Table V. IEH Atomic Charges

molecule	atom	charges[a]
S_2P	S	0.171 (0.176)
	N	−0.258 (−0.299)
	C_2	−0.048 (−0.044)
	C_3	0.009 (0.018)
	C_4	−0.026 (−0.025)
	C_5	0.010 (0.002)
	C_6	−0.056 (−0.062)
	H_1	0.049 (0.053)
	H_2	0.064 (0.073)
	H_3	0.041 (0.048)
Se_2P	Se	0.245 (0.249)
	N	−0.247 (−0.289)
	C_2	−0.065 (−0.055)
	C_3	−0.020 (0.000)
	C_4	−0.038 (−0.030)
	C_5	0.002 (−0.002)
	C_6	−0.064 (−0.069)
	H_1	0.057 (0.056)
	H_2	0.069 (0.070)
	H_3	0.059 (0.049)
SSeP	S	0.146 (0.141)
	Se	0.247 (0.244)
	N	−0.231 (−0.271)

[a] Charges with d orbitals (in parentheses, without d orbitals).

In summary, the issue as to whether Se_2TPP^+ is a σ^* radical while S_2TPP^+ is a π radical remains unsettled to the authors. In any event, our discussion raises the possibility that for Se_2TPP^+ both a π and a Se(σ^*) radical are possible. One or the other might be more favored in different conditions, i.e., change of solvent or temperature; hence, experimental effort to seek both kinds of radicals would seem useful. In this regard it should be noted that in the $NiTPP^+$ radical cation a thermal equilibrium between a π radical and a d_{z^2} radical has been found;[34] moreover, σ^* radicals are known between two sulfur atoms.[35]

E. Charge-Transfer Band Shift in the Protonated Dications. To further substantiate the CT hypothesis, the absorption and emission of the conjugate acids were studied. Since the CT state in Se_2TPP and SSeTPP corresponds to a large intramolecular charge separation with a large positive charge on the Se, and since the ground-state HOMO is localized on the Se, the CT transition should be shifted to higher energy when the porphyrin core is protonated. This idea is in good agreement with the curve-fitted absorption spectra, in that the same number of Gaussians are required for the four molecules H_2TPP, S_2TPP, SSeTPP, and Se_2TPP in a benzene/TFA mixture. Although this result suggests that the CT state is shifted to higher energy in the conjugate acids, there is no room-temperature emission from Se_2TPP and SSeTPP in an acidic solution. The reason for this is unclear.

F. IEH Results on the Conjugative Pathway. The conjugative pathways in the chalcogen porphyrins have recently been discussed in connection with the interpretation of the ^1H NMR.[1a] Thus the exo protons of the pyrrole, thiophene, and selenophene rings have δ 8.90, 9.68, and 9.89 in H_2TPP, S_2TPP, and Se_2TPP. The pyrrolenine δ values for the exo protons are 8.61, 8.68, and 8.86, respectively. The shifts in δ from pyrrole to thiophene and selenophene were attributed to the cross-ring bonding S–S, S–Se, and Se–Se.[1a] This bonding was presumed to shift the ring current from the inner to the outer ring, thus explaining the strong downfield shift (i.e., increased δ) compared to that of pyrrole.

In Table IV we list the bond orders for the pyrrole, thiophene, and selenophene rings as well as for the inner-

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great-ring pathway through the pyrrolenine ring. Table IV includes comparison bond orders for a Pariser–Parr–Pople calculation of H_2P.[36] Presumably increased outer-ring current would be manifested by the bond orders $C_1–C_2$ and $C_2–C_3$ coming closer to the average bond order for the 18-membered great ring while the bond order $X–C_3$ (X = S or Se) becomes much smaller. No such clear trends appear in the bond-order data.

The calculations offer another explanation for the observed δ value shifts: i.e., the change in charge of the hydrogen atoms listed in Table V. It can be seen that the H_1 and H_3 atoms are distinctly less positive in S_2TPP than in Se_2TPP, implying greater shielding (i.e., smaller δ value) in S_2TPP.

Summary Discussion

The emission data and theoretical analysis by the IEH model on S_2TPP, SSeTPP, and Se_2TPP have led to several conclusions: (1) The Se compounds but not S_2TPP contain an allowed low-energy charge-transfer band $Se(4p_y) \rightarrow b_{2g}(\pi^*)$. This excited state explains the lack of emission in the Se complexes and is apparent when the first absorption band is curve fit by Gaussians. (2) The calculations suggest the possibility that Se_2TPP^+ may be either a π or a $Se(\sigma^*)$ radical. While Fajer and Richardson[28] believe that their Se_2TPP^+ is a π radical, we believe that their data may also be interpreted as a $Se(\sigma^*)$ radical. In any event, it may be possible to find both types of radical under the proper conditions. (3) The X-ray structures of these species[5] can only be understood if contracted d orbitals are included in the IEH calculations; for only then do the calculations show increased bonding between the group 6 atoms across the core in the order $S_2P < SSeP < Se_2P$. (4) Bond-order analysis of the conjugative pathway does not support the view that the shift to higher δ values of the thiophene and selenophene exo protons is due to a shift of the ring current from the inner to the outer rings;[1] possibly charge density differences may account for this phenomenon.

The most compelling study that would confirm or refute our view would be a polarized absorption study of the far-red absorption band of these compounds. Such study should show z-polarized absorption in the red tail of SSeTPP and Se_2TPP but not in S_2TPP or the protonated species, where z-polarized absorption may appear further to the blue. Although we found no evidence for phosphorescence, the triplet state should be populated in S_2TPP and its acid dication, both of which show fluorescence. The triplet state may not be populated in SSeTPP and Se_2TPP, where decay to the ground state passes through a charge-transfer state. Transient absorption studies are necessary if a long-lived triplet state is to be found. Finally we note that the study of $^{33}S_2TPP^+$ could provide confirmation of our hypothesis that the unpaired electrons in S_2TPP^+ and in Se_2TPP^+ are in different orbitals.

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Registry No. S_2TPP, 57511-57-6; SSeTPP, 66951-07-3; Se_2TPP, 66951-06-2; $S_2TPPH_2^{2+}$, 80376-65-4.

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Electronic Spectroscopy of Diphosphine and Diarsine Complexes of Rhodium(I) and Iridium(I)

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The electronic absorption spectra at room temperature, emission and excitation spectra at 77 K, and emission lifetimes at 77 K have been measured for complexes with the general formulas $[M(L–L)_2]^+$ and $[M(L–L)(1,5\text{-cyclooctadiene})]^+$ [M = Rh(I), Ir(I); L–L = diphosphines, diarsine, mixed phosphine–arsine]. For a given metal, the absorption and excitation band energies are relatively insensitive to all the ligands except 1,5-cyclooctadiene. The $\sim$2500-cm^{-1} red shift of the spectral features of the comlexes containing 1,5-cyclooctadiene is attributed to destabilization of all the d orbitals due to closer approach of the diphosphine ligand to the metal center. The low-temperature (1.8–90 K) emission spectral and lifetime data are interpreted in terms of a two-level spin–orbit split triplet manifold. The charge-transfer vs. metal-localized character of the low-energy excited states is discussed.

Introduction

The electronic spectroscopy of Rh(I) and Ir(I) complexes containing ligands such as CO, CN^-, CNR, AsR_3, PR_3, and bidentate diphosphines has been the subject of numerous reports.[1-8] Prototypes for these studies are $[M(L–L)_2]^+$ ions [M = Rh(I), Ir(I); L–L = diphos or 2=phos[9]], whose intense photoluminescence and that of complexes containing other

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