reported. Oxidation of most of the stilbenes is irreversible, and peak potentials are reported.

Transient Spectroscopy. Acetonitrile solutions of DCA or TCA (10^{-5} M) were excited at 410 nm in the presence of various electron donors with an excimer-pumped (Questek 2000) Lumonics Model EPD-330 dye laser (DPS dye, ca. 15-ns pulses, 2 mJ/pulse). Transient absorption spectra of the stilbene cation radicals are obtained either directly, via electron-transfer quenching by stilbene (0.1 M), or indirectly, via primary quenching by biphenyl (0.15 M) followed by secondary electron transfer from stilbene (5×10^{-4} M) to the biphenyl cation radical. The overlapping absorption of DCA$^{\bullet-}$ can be removed by means of irradiation in the presence of oxygen, which is reduced by DCA$^{\bullet-}$, forming superoxide, which is transparent in the visible region. Extinction coefficients were determined with the cation radical of tritolylamine (λ_{max} = 668 nm, ϵ = 26 200[15]), generated under identical secondary electron transfer conditions, as an actinometer. All spectra were recorded 0.5 μs after the excitation pulse.

Relative quantum yields for the formation of free stilbene cation radicals were determined by means of electron-transfer quenching of singlet DCA or TCA by stilbene (0.05 M) followed by secondary electron transfer from the stilbene cation radical to *trans*-4,4′-dimethoxystilbene. Absolute quantum yields were obtained from the triplet state of benzophenone as an actinometer.

Singlet lifetimes were measured by time-correlated single photon counting in argon-purged acetonitrile solutions. Lifetimes were independent of cyanoanthracene concentration (10^{-5}–10^{-6} M).

Note Added in Proof. Subsequent to the completion of this paper, the formation of low yields of stilbene dimers has been observed from both the chemical oxidation (N. L. Bauld, University of Texas, Austin, private communication) and the photochemical oxidation of *trans*-stilbene (B. A. Winset, Northwestern University, unpublished results). These observations lend credence to the proposed formation of the stilbene dimer cation radical (eq 3).

Acknowledgment. We thank J. Harrelson, Jr., and A. V. Satish for the electrochemical measurements and C. Amatore for informing us of his electrochemical results. Work performed at Northwestern University is supported by the National Science Foundation (Grant CHE-8618994).

Appendix I

Thermochemical Estimates. The enthalpy of reaction for addition of t-S$^{\bullet+}$ and c-S to form an acyclic cation radical is estimated from the thermochemical cycle shown in Scheme VI (energies in kilocalories per mole). The oxidation potential of t-S is from Table III, and that of the diyl is assumed to be the same as for the 1-phenylethyl radical.[46] The diyl bond dissociation energy can be estimated either by consideration of the energies of the bonds being broken (C–C: 65 kcal/mol) and formed (C=C: t-S = 39, c-S = 35 kcal/mol) or by means of Benson group additivity calculations.[47,48] The resultant value of $\Delta H° = -18$ kcal/mol can be corrected for the loss of translational energy in a typical dimerization reaction ($\Delta S° \sim -35$ eu or +10 kcal/mol)[49] to provide a value of $\Delta G° = -8$ kcal/mol.

The enthalpy of reaction for ring opening of TPCB$^{\bullet+}$ can be estimated from the thermochemical cycle shown in Scheme VII (energies in kilocalories per mole). The oxidation potential of TPCB was determined in the present investigation while that of the diyl is assumed to be the same as for the 1-phenylethyl radical.[46] The TPCB bond dissociation energy is assumed to be the same as that of several other 1,2-diarylcyclobutanes.[50] The resultant value of $\Delta H°$ is −7 kcal/mol.

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Synthesis and Photoproperties of Diamagnetic Octabutoxyphthalocyanines with Deep Red Optical Absorbance

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Abstract: The synthesis and photoproperties of six new metal 1,4,8,11,15,18,22,25-octabutoxyphthalocyanines and photoproperties of the known, analogous Zn and metal-free phthalocyanines are described. The new compounds are $AlPc(OBu)_8OSiEt_3$, $GaPc(OBu)_8OSiEt_3$, $GePc(OBu)_8(OSiEt_3)_2$, $SnPc(OBu)_8(OSiEt_3)_2$, $RuPc(OBu)_8(py)_2$, and $PdPc(OBu)_8$ (where $Pc(OBu)_8$ represents the octabutoxyphthalocyanine ligand). Benzene-d_6 solutions of all eight of the compounds give NMR spectra showing large ring-current effects. Benzene solutions of the compounds give visible spectra with absorption maxima in the 688–779-nm range having extinction coefficients between 1.0×10^5 and 2.2×10^5 M^{-1} cm^{-1}. The triplet-state properties of the phthalocyanines in benzene solutions have been measured by laser flash photolysis. The triplet states have absorption maxima in the 550–640-nm range, quantum yields in the 0.1–0.9 range, and lifetimes when the solutions are deaerated in the 0.5–150-μs range. The rate constants for energy transfer from the triplet states of the compounds to O_2 are between 1.3×10^8 and 2.8×10^9 M^{-1} s^{-1}. Analysis of kinetic data pertaining to the photogeneration of O_2 ($^1\Delta_g$) by the main-group compounds shows that the energy gap between their singlet (S_1) and triplet (T_1) states is 14.9 ± 0.3 kcal/mol. Relationships between the photoproperties of the metal complexes and the position in the periodic chart of the metals they contain are apparent.

Introduction

The 1,4,8,11,15,18,22,25-octaalkoxyphthalocyanines (Figure 1) generally are stable compounds that have intense absorptions in the red to deep red region.[1] This suggests that some of them have potential for use in optical data storage[2] and in photodynamic therapy, PDT.[3]

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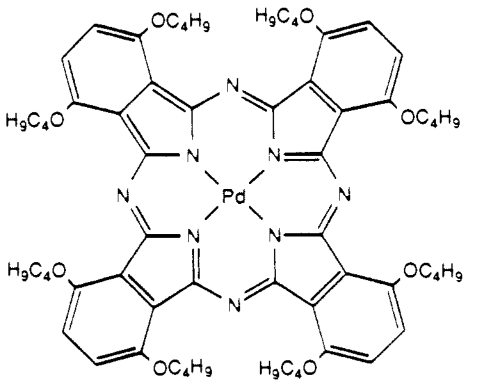

Figure 1. Palladium 1,4,8,11,15,18,22,25-octa-*n*-butoxyphthalocyanine. The analogous Al and Ga complexes have one axial $OSiEt_3$ group, the Ge and Sn complexes have two trans $OSiEt_3$ axial groups, and the Ru complex has two trans pyridyl groups.

As part of our work on PDT, we recently carried out a study on the photoproperties of the metal-free and Zn members of this family.[4] This study shows that the Zn complex is a potent photogenerator of O_2 ($^1\Delta_g$).

In a continuation of this study, we have now prepared, purified, and characterized six new metal 1,4,8,11,15,18,22,25-octabutoxyphthalocyanines. The photoproperties of these new compounds have been examined, and in addition, the photoproperties of their metal-free and Zn analogues have been reexamined. From the data gathered, relationships have been found between the photoproperties of the metal complexes and the position in the periodic table of the metals they contain. These trends are compared to analogous relationships found for metal porphyrins and phthalocyanines.[5] The results of this work continue to point to the potential of selected octaalkoxyphthalocyanines for PDT.

Experimental Section

$H_2Pc(OBu)_8$. This procedure is patterned after a procedure for $H_2Pc(OBu)_8$ by Cook and co-workers:[1] Under Ar, Li (1.1 g) was added in portions to a refluxing suspension of 1,4-dibutoxy-2,3-dicyanobenzene (4.5 g) in dry 1-BuOH (30 mL), and the resulting mixture was refluxed for 1 h and cooled. The suspension formed was diluted with glacial HOAc (200 mL), and the resultant mixture was stirred for 1 h and then evaporated to dryness with a rotary evaporator (80 °C). The residue was dissolved in CH_2Cl_2 (200 mL), and the solution was washed twice with dilute HCl (10%), four times with H_2O, dried ($MgSO_4$), and evaporated to dryness with a rotary evaporator (40 °C). The residue was successively chromatographed (Al_2O_3 V, 4 × 12 cm, pyridine), washed (MeOH), recrystallized (CH_2Cl_2–MeOH solution). vacuum dried (60 °C), and weighed (1.4 g, 30%). Mp: 222–3 °C (lit.[6] mp 136.5–138.5 °C). NMR: δ 7.53 (s, 2,3-Pc H), 4.91 (t, α-Bu CH_2), 2.20 (m, β-Bu CH_2), 1.70 (m, γ-Bu CH_2), 1.03 (t, Bu CH_3), 0.08 (s, NH). Anal. Calcd for $C_{64}H_{82}N_8O_8$: C, 70.41; H, 7.57; N, 10.26. Found: C, 70.33; H, 7.28; N, 10.16. MS-HRFAB exact mass *m/z* for $C_{64}H_{82}N_8O_8$ $(M)^+$: calcd, 1091.6334; found, 1091.6334. UV–vis (benzene) (λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 327, 57 000; 762, 135 000. Fluorescence (benzene) (λ_{max} (nm)): 778.

$ZnPc(OBu)_8$. $ZnPc(OBu)_8$ was prepared by the procedure of Cook and co-workers.[1] Mp: >250 °C. NMR: δ 7.58 (s, 2,3-Pc H), 5.06 (t, α-Bu CH_2), 2.23 (m, β-Bu CH_2), 1.71 (m, γ-Bu CH_2), 1.03 (t, Bu CH_3). MS-HRFAB exact mass *m/z* for $C_{64}H_{81}N_8O_8Zn$ $(M + H)^+$: calcd, 1153.5469; found, 1153.5423. UV–vis (benzene; 1% pyridine) (λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 324, 43 000; 661, 39 000; 737, 190 000. Fluorescence (benzene; 1% pyridine) (λ_{max} (nm)): 752.

$AlPc(OBu)_8OSiEt_3$. A mixture of $H_2Pc(OBu)_8$ (110 mg), an $AlMe_3$–toluene solution (25%, 0.25 mL), and toluene (12 mL) was stirred under Ar for 30 min and cooled (ice bath). Water (1 mL) and toluene (10 mL) were added to the resulting solution, and the suspension formed was dehydrated by distillation (ca. 5 mL of distillate).

A mixture of the dehydrated suspension, Et_3SiOH (0.050 mL), and pyridine (1 mL) was refluxed for 2 h and cooled. The resultant was filtered (diatomaceous earth bed) and evaporated to a solid with a rotary evaporator (70 °C). The solid was dissolved in toluene (ca. 3 mL), and the solution was evaporated to a solid. This solid was repeatedly chromatographed (Bio-Beads S-X4 (Bio-Rad Laboratories), 2 × 50 cm, toluene), vacuum dried (60 °C), and weighed (40 mg, 32%). Mp: 114–6 °C. NMR: δ 7.58 (s, 2,3-Pc H), 4.94 (m, α-Bu CH_2), 2.20 (m, β-Bu CH_2), 1.71 (m, γ-Bu CH_2), 1.05 (t, Bu CH_3), –0.44 (t, Et CH_3), −1.34 (q, Et CH_2). MS-HRFAB exact mass *m/z* for $C_{70}H_{95}H_8O_9AlSi$ $(M)^+$: calcd, 1246.6807; found, 1246.6839. UV–vis (benzene) (λ_{max} (nm), ϵ (M^{-1} cml–^{1})): 332, 62 000; 682, 39 000; 764, 190 000. Fluorescence (benzene) (λ_{max} (nm)): 787.

$GaPc(OBu)_8OSiEt_3$. A mixture of $H_2Pc(OBu)_8$ (110 mg), $GaCl_3$ (79 mg), and dry dimethylformamide (10 mL) was refluxed after Ar for 20 min and cooled. The solution formed was diluted with CH_2Cl_2 (40 mL), treated twice with dilute HCl (10%, 30 mL each time), and treated three times with H_2O (30 mL each time). The treated solution was dried ($MgSO_4$) and evaporated to a solid with a rotary evaporator (40 °C). This solid was chromatographed (Al_2O_3 V, 2 × 8 cm, 8:2 CH_2Cl_2–methanol), rechromatographed (Bio-Beads S-X4, 2 × 50 cm, toluene), and weighed (64 mg).

A mixture of the chromatographed solid (60 mg), Et_3SiOH (0.10 mL), pyridine (1 mL), and toluene (10 mL) was slowly distilled for 2.5 h (3 mL of distillate), and the solution formed was evaporated to a solid with a rotary evaporator. This solid was chromatographed (Bio-Beads S-X4, 2 × 50 cm, toluene), vacuum dried (70 °C), and weighed (62 mg, 53%). Mp: 125–7 °C. NMR: δ 7.56 (s, 2,3-Pc H), 4.96 (m, α-Bu CH_2), 2.17 (m, β-Bu CH_2), 1.70 (m, γ-Bu CH_2), 1.02 (t, Bu CH_3), –0.48 (t, Et CH_3), −1.36 (q, Et CH_2). MS-HRFAB exact mass *m/z* for $C_{70}H_{95}N_8O_9{}^{69}Ga^{28}Si$ $(M)^+$: calcd, 1228.6247; found, 1228.6275. UV–vis (benzene; 1% pyridine) (λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 335, 62 000; 685, 44 000; 767, 205 000. Fluorescence (benzene; 1% pyridine) (λ_{max} (nm)): 786.

$GePc(OBu)_8(OSiEt_3)_2$. $GeCl_4$ (0.250 mL) was added in five portions over a 5-h period to a mixture of $H_2Pc(OBu)_8$ (215 mg), $GeCl_4$ (0.150 mL), and dry dimethylformamide (20 mL) that was being refluxed under Ar. The solution formed was cooled, diluted with CH_2Cl_2 (40 mL), treated twice with dilute HCl (10%, 30 mL each time), and treated three times with H_2O (30 mL each time). The treated solution was dried ($MgSO_4$) and evaporated to a solid with a rotary evaporator (40 °C). This solid was chromatographed (Al_2O_3 V, 1.5 × 15, 1:1 toluene–pyridine), and weighed (141 mg).

A mixture of the chromatographed solid, Et_3SiOH (0.10 mL), pyridine (1.5 mL), and toluene (10 mL) was refluxed for 2.5 h, and the solution formed was evaporated to a solid with a rotary evaporator (70 °C). The solid was chromatographed (Bio-Beads S-X4, 2 × 50 cm, toluene), vacuum dried (75 °C), and weighed (110 mg, 40%). Mp: 147–9 °C. NMR: δ 7.54 (s, 2,3-Pc H), 4.98 (t, α-Bu CH_2), 2.18 (m, β-Bu CH_2), 1.67 (m, γ-Bu CH_2), 1.00 (t, Bu CH_3), −0.78 (t, Et CH_3), −1.82 (q, Et CH_2). MS-HRFAB exact mass *m/z* for $C_{76}H_{110}N_8O_{10}{}^{70}GeSi_2$ $(M)^+$: calcd, 1420.7126; found, 1420.7092. UV–vis (benzene) (λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 333, 65 000; 679, 46 000; 761, 215 000. Fluorescence (benzene) (λ_{max} (nm)): 775.

$SnPc(OBu)_8(OSiEt_3)_2$. A mixture of $H_2Pc(OBu)_8$ (200 mg), $SnCl_4\cdot 5H_2O$ (456 mg), and dimethylformamide (10 mL) was refluxed under Ar for 1 h and cooled. The resulting suspension was filtered, and the solid was washed with toluene (5 mL) and pentane (10 mL), air dried (25 °C), and weighed (92 mg).

A mixture of Et_3SiOH (0.10 mL), Na (5 mg), and *p*-xylene (10 mL) was refluxed under Ar for 3 h and slightly cooled. Solid from the first step (90 mg) was added to the solution formed, and the mixture was refluxed for 10 min. The resultant was washed three times with H_2O (30 mL each time), dried ($MgSO_4$), and evaporated to a solid with a rotary evaporator (85 °C). This solid was chromatographed (Bio-Beads S-X4, 2 × 50 cm, toluene), vacuum dried (60 °C), and weighed (65 mg, 25%). Mp: 133–5 °C. NMR: δ 7.52 (s, 2,3-Pc H), 4.97 (t, α-Bu CH_2), 2.16 (m, β-Bu CH_2), 1.65 (m, γ-Bu CH_2), 1.00 (t, Bu CH_3), −0.71 (t, Et CH_3), −1.68 (q, Et CH_2). MS-HRFAB exact mass *m/z* for $C_{70}H_{95}N_8O_9{}^{116}SnSi$ $(M - SiOEt_3)^+$: calcd 1335.6009; found, 1335.6009. UV–vis (benzene) (λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 337, 60 000; 695, 44 000; 779, 185 000. Fluorescence (benzene) (λ_{max} (nm)): 798.

$PdPc(OBu)_8$. A mixture of $H_2Pc(OBu)_8$ (134 mg), $PdCl_2(PPh_3)_2$ (230 mg), and dimethylformamide (8 mL) was refluxed under Ar for 1

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[6] The purification procedure used earlier[1] is not stated.

h and cooled. The solution formed was diluted with CH_2Cl_2 (40 mL), washed twice with dilute HCl (10%, 30 mL each time), washed three times with H_2O (30 mL each time), dried ($MgSO_4$), and evaporated to a solid with a rotary evaporator (40 °C). This solid was chromatographed (Bio-Beads S-X4, 2 × 50 cm, toluene), vacuum dried (60 °C), and weighed (65 mg, 45%). Mp: 143–5 °C. NMR: δ 7.53 (s, 2,3-Pc H), 4.97 (t, α-Bu CH_2), 2.21 (m, β-Bu CH_2), 1.70 (m, γ-Bu CH_2), 1.04 (t, Bu CH_3). MS-HRFAB exact mass m/z for $C_{64}H_{81}N_8O_8{}^{106}Pd$ $(M + H)^+$: calcd, 1195.5213; found, 1195.5231. UV-vis (benzene) (λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 321, 47000; 648, 44000; 724, 200000. Fluorescence (benzene) (λ_{max} (nm)): 743.

$RuPc(OBu)_8(py)_2$. A mixture of $H_2Pc(OBu)_8$ (261 mg), $Ru_3(CO)_{12}$ (181 mg), and dry pyridine (130 mL) was refluxed under Ar for 3 h and cooled. The suspension formed was filtered (Florisil bed (Fisher Scientific)), the filter bed was washed with pyridine (100 mL), and the filtrate and washings were combined.

While it was being purged with Ar, the solution was irradiated with a Hg lamp (medium pressure, 450 W) for 20 h. The resultant was evaporated to a solid with a rotary evaporator (75 °C). This solid was chromatographed (Al_2O_3 I, 1.5 × 8 cm, EtOAc and then warm pyridine), recrystallized (toluene), vacuum dried (60 °C), and weighed (60 mg, 20%). Mp: >260 °C. NMR: δ 7.36 (s, 2,3-Pc H), 5.04 (t, α-Bu CH_2), 2.20 (m, β-Bu CH_2), 1.63 (m, γ-Bu CH_2), 0.96 (t, Bu CH_3), 4.91 (m, 4-py H), 4.08 (m, 3,5-py H), 2.71 (m, 2,6-py H). UV-vis (benzene) (λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 312, 92000; 624, 47000; 688, 97000. Fluorescence (benzene) (λ_{max} (nm)): 750.

Solubility and Color. All of the compounds are soluble (≥1 mg/mL) in CH_2Cl_2, all but $RuPc(OBu)_8(py)_2$ in toluene, and all but $RuPc(OBu)_8(py)_2$ and $PdPc(OBu)_8$ in hexanes. All are green except for $RuPc(OBu)_8(py)_2$, which is blue.

NMR Spectra. The NMR spectra were taken with a 200-MHz spectrophotometer (Varian Associates, XL-200) at 50 °C. The solvent used was benzene-d_6, and the sample concentrations were about 7 mM.

Photoproperties. The ground-state absorption spectra were measured with a diode array spectrophotometer (Perkin-Elmer, Lambda Array 3840) operated in the high-resolution mode (0.25 nm). Steady-state red–infrared luminescence spectra were measured with an apparatus described earlier.[7] An Ar ion laser (Coherent, Innova 90) with multiline output (principal lines at 514.5 and 488 nm) was used for excitation. The emission spectra were not corrected for the wavelength dependence of the sensitivity of the germanium diode detector.

Time-resolved triplet–triplet absorption and IR luminescence measurements were made with improved versions of systems described earlier.[8] A Q-switched Nd:YAG laser (Quantel, YG-571-C) operating at either the second (532 nm) or third (355 nm) harmonic was employed for excitation. Typically, data from 5 to 10 replicate shots were signal-averaged for kinetic analysis. The O_2 concentrations of the phthalocyanine solutions were varied by passing Ar or O_2, or custom-made O_2–N_2 mixtures (Airco, analyzed), through the solutions. The Ar was passed through an O_2 trap (Alltech Associates) in order to reduce the concentration of O_2 to less than 0.1 ppm. The concentrations of O_2 were calculated on the basis of Henry's law, with the concentration of O_2 in air-saturated benzene taken to be 1.91×10^{-3} M.[9] All measurements were made at ambient temperature (23 ± 2 °C) except for the low-temperature phosphorescence measurements.

Values for the product of the quantum yields of the triplet states of the phthalocyanines and their triplet minus ground-state extinction coefficient differences, $\Phi_T\Delta\epsilon_T$, and values for the quantum yields of O_2 $(^1\Delta_g)$, Φ_Δ, were obtained by the relative method[10] with excitation at 355 nm. Benzene was used as the solvent, and solutions of benzophenone in benzene or benzene-d_6 were used as standards. For these standards, the value of $\Phi_T\Delta\epsilon_T$ was taken as 7220 M^{-1} cm^{-1} at 532 nm[11] and the value of Φ_Δ was taken as 0.27.[12] The phthalocyanine concentrations used were generally in the range of 10–30 μM. This resulted in absorbances at 355 nm of 0.3–0.7/cm of path length. Laser intensities were adjusted so as to limit the ground-state depletions to less than 25%.

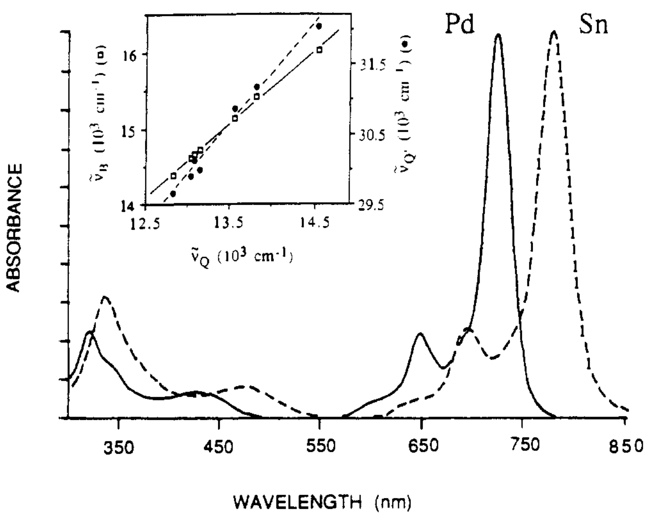

Figure 2. Ground-state electronic absorption spectra of $PdPc(OBu)_8$ (—) and $SnPc(OBu)_8(OSiEt_3)_2$ (---) in benzene. The spectra are normalized to the same absorbance at the Q(0,0) band maxima. Inset: Linear dependence of the frequency of the B-band (□) and Q′-band (●) maxima on the frequency of the Q(0,0) maxima for the metal octabutoxyphthalocyanines in benzene solution. By linear-regression analysis, the slope of the line is 1.44 and the intercept is 11.23×10^3 cm^{-1} for the B band and the slope of the line is 0.972 and the intercept is 1.95×10^3 cm^{-1} for the Q′ band.

Values of $\Delta\epsilon_T$ for all but the Ru and Pd complexes were determined by the energy-transfer method,[10] and protoporphyrin IX dimethyl ester, PPDME, as the triplet-energy donor and with 532-nm laser excitation. The value of $\Delta\epsilon_T$ for PPDME was taken as 30500 M^{-1} cm^{-1} at 450 nm.[13] Before the phthalocyanine was added, the laser intensity was adjusted so that the decay of the triplet state of PPDME was exponential. Under these conditions, the lifetime of the triplet state was 150 μs. The concentrations of the phthalocyanines were in the range 20–40 μM. This range was sufficient for a probability of energy transfer of >80% and a ground-state absorbance at 532 nm of the phthalocyanine that was small relative to that of PPDME. Phthalocyanine triplet-state formation and decay kinetics were monitored at 590 nm, where absorbance changes due to the PPDME triplet were negligible and the ground-state extinction coefficients of the phthalocyanines were relatively small. Although the ground-state absorbances of the phthalocyanines at 532 nm were small compared to the absorbance of PPDME, detectable triplet-state formation usually occurred as a result of direct photoexcitation. This population was readily distinguished kinetically from that due to energy transfer, and only absorption changes due to the latter process were used in calculating $\Delta\epsilon_T$. The bimolecular rate constants for energy transfer were in the range 1.6×10^9–1.9×10^9 M^{-1} s^{-1} for the metal complexes. The rate constant for the metal-free compound was somewhat higher, 2.8 × 10^9 M^{-1} s^{-1}.

The total depletion method[10] was used to obtain values of $\Delta\epsilon_T$ for the Ru and Pd complexes because of their short triplet-state lifetimes, τ_T. This method was also used to obtain a second value for $\Delta\epsilon_T$ for the Sn complex since this compound has a moderately short τ_T. The laser excitation wavelength was 355 nm, and the phthalocyanine concentrations used were 3–8 μM. The values determined by this technique were independent of concentration in this range.

Results

Ground-State Absorption Spectra. The UV-visible absorption spectra of benzene solutions of the metal complexes have Q(0,0) maxima, ranging from 688 nm in the case of $RuPc(OBu)_8(py)_2$ to 779 nm in the case of $SnPc(OBu)_8(OSiEt_3)_2$. The extinction coefficients, ϵ_{max}, are close to 2×10^5 M^{-1} cm^{-1} for all the metal complexes except for the Ru complex. For this complex, ϵ_{max} is half as large. The absorption spectra of the Pd and Sn complexes, shown in Figure 2, have patterns that typify those of the metal complexes. Besides the far-red Q(0,0) band, the spectra have maxima in the regions of 620–700, 390–480, and 310–340 nm. By analogy to assignments made for zinc phthalocyanine, the phthalocyanine for which spectral assignments are most firmly

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(8) (a) Rodgers, M. A. J. In *Primary Photo-Processes in Biology and Medicine*; Bensasson, R. V., Jori, G., Land, E. J., Truscott, T. G., Eds.; Plenum: New York, 1985; pp 1–23. (b) Rodgers, M. A. J.; Snowden, P. T. *J. Am. Chem. Soc.* **1982**, *104*, 5541–5543.

(9) Murov, S. *Handbook of Photochemistry*; Dekker: New York, 1973; p 89.

(10) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1988**, *15*, 1–250.

(11) Hurley, J. K.; Sinai, N.; Linschitz, H. *Photochem. Photobiol.* **1983**, *38*, 9–14.

(12) Gorman, A. A.; Hamblett, I.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1984**, *106*, 4679–4682. This value reflects the fact that the benzophenone triplet is 94% quenched by O_2 in air-saturated benzene.

(13) Sinclair, R. S.; Tait, D.; Truscott, T. G. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 417–425.

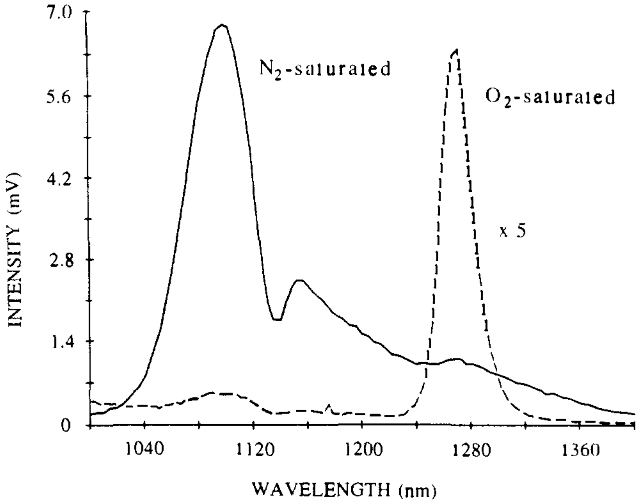

Figure 3. Phosphorescence spectra of benzene solutions of $PdPc(OBu)_8$ saturated with N_2 (—) and O_2 (---). The emission at 1270 nm in the O_2-saturated solution is from O_2 ($^1\Delta_g$).

established,[14] the band in the 620–700-nm region (referred to here as the Q′ band), is assigned to an admixture of the Q(2,0) vibronic satellite and an additional electronic transition.[14] Similarly, the band in the 310–340-nm region is assigned to the B-band transition. The band in the 390–480-nm region has no immediately obvious assignment. The inset in Figure 2 shows that the frequencies of the Q′ and B bands shift in parallel with the Q(0,0) band within the series of metal octabutoxyphthalocyanines.

The absorption spectrum of $GaPc(OBu)_8OSiEt_3$ in pure benzene has a relatively weak maximum near 815 nm in addition to the main band at 767 nm. This extra band disappears upon the addition of pyridine, with the concomitant growth of the 767-nm band. We attribute the 815-nm band to the existence of a face-to-face dimer or some other aggregate in accordance with our earlier assignment for solutions of the Zn complex.[4] The photoproperties of the Ga and Zn complexes were measured in benzene containing pyridine (1%, by volume) in order to prevent this aggregation. The same solvent mixture was used with the Ru complex to prevent ligand loss.[15] Low concentrations of pyridine have no effect on the spectral properties of the other phthalocyanines. It is possible that $ZnPc(OBu)_8$ exists as a monopyridine adduct under the conditions used.[16]

Emission Spectra. The fluorescence spectra of benzene solutions of the phthalocyanines have maxima attributable to the Q(0,0) and Q′ transitions. The Q′ maxima are, in each case, ca. 1300 cm^{-1} (3.8 kcal/mol) to the red of the Q(0,0) maxima. The Q(0,0) transition of $RuPc(OBu)_8(py)_2$ has a larger Stokes shift, 3.4 kcal/mol, than the Q(0,0) transitions of other compounds, 0.7–1.1 kcal/mol.

The Ru and Pd complexes exhibit an additional emission in deaerated solutions. This emission is assigned to phosphorescence because its intensity decreases substantially when the solution is saturated with O_2 and because the 1270-nm emission of O_2 ($^1\Delta_g$) appears when this is done. Figure 3 shows spectra obtained from a solution of $PdPc(OBu)_8$ in benzene under these two conditions. The $T_1(0,0)$ emission maxima (±5 nm) are at 910 and 1100 nm for the ruthenium and palladium phthalocyanines, respecively. The apparent second maximum near 1150 nm in the phosphorescence spectrum of $PdPc(OBu)_8$ is an artifact that may have been caused by an absorption in the region near 1130 nm arising from silica in the apparatus. None of the other phthalocyanines give unambiguous evidence of phosphorescence in the range 900–1400 nm in N_2-saturated benzene (23 °C) or in 2-methyltetrahydrofuran glass (77 K).[17,18]

Table I. Triplet-State Properties of Octabutoxyphthalocyanines in Benzene[a]

	Z	$\lambda^{max\,b}$ (nm)	$\Delta\epsilon_T{}^c$ (10^4 M^{-1} cm^{-1})	$\Phi_T{}^d$	$\tau_T{}^e$ (μs)
H_2	1	610	4.5	0.10	17
Al^{III}	13	620	3.8	0.23	135
Zn^{II}	30	615	3.7	0.48	63
Ga^{III}	31	620	4.1	0.35	67
Ge^{IV}	32	620	3.5	0.32	150
Ru^{II}	44	550	0.83[f]	0.88	0.53
Pd^{II}	46	620	2.8[f]	0.77	3.5
Sn^{IV}	50	640	2.0, 2.7[f]	0.56	25

[a] Pyridine (1%) was added to the solutions of the Zn, Ga, and Ru complexes. [b] ±5 nm. [c] Monitored at 550 nm with the Ru complex and 590 nm with the rest; ±10%. [d] ±20%. [e] In deaerated solution, ±5%. [f] By the total depletion technique.

Table II. Octabutoxyphthalocyanine Triplet-State Quenching by O_2 and O_2 ($^1\Delta_g$) Formation and Decay in Benzene[a]

	$k_{T\Sigma}{}^b$ (M^{-1} s^{-1})	$\Phi_\Delta{}^c$	$\tau_\Delta{}^d$ (μs)
H_2	1.3×10^8	<0.05	<50
Al^{III}	5.7×10^8	0.30	100
Zn^{II}	1.8×10^9	0.47	290
Ga^{III}	4.5×10^8	0.41	85
Ge^{IV}	1.3×10^9	0.33	280
Ru^{II}	2.1×10^9	0.42[e]	380
Pd^{II}	2.8×10^9	0.64	440
Sn^{IV}	4.2×10^8	0.56	55

[a] Φ_Δ and τ_Δ were obtained from benzene-d_6 solutions. Pyridine (1%) was added to the solutions of the Zn, Ga, and Ru complexes; ±5%. [b] ±5%. [c] Air-saturated solutions; ±15%. [d] ±15%. [e] A value of 0.53 was attained on O_2 saturation.

Triplet-State Yields and Lifetimes. Laser flash photolysis of solutions of the phthalocyanines produce transients that are identified as being due to triplet, T_1, states because they are quenched by O_2 and because they can be formed via the T_1 state of PPDME. Table I gives a summary of the properties found for these triplet states. As is seen, the maxima in the difference absorption spectra of the triplets, $\lambda_T{}^{max}$, of all the complexes but the Ru complex range from 610 to 640 nm, the triplet state quantum yields, Φ_T, range from 0.1 to 0.9, and the triplet lifetimes, τ_T, in deaerated solutions range from 0.5 to 150 μs.

Triplet-State Quenching by O_2. Quenching of the T_1 states of the phthalocyanines by O_2 results in the formation of O_2 ($^1\Delta_g$). Table II summarizes parameters associated with the formation and decay of the singlet O_2 formed. The rate constants $k_{T\Sigma}$ in this table are the bimolecular rate constants for energy transfer from the phthalocyanine (T_1) to O_2 ($^3\Sigma_g{}^-$). For the zinc, ruthenium, and palladium phthalocyanines, exponential triplet-decay kinetics are observed in air- and O_2-saturated solutions. In these cases, the first-order rate constant, k_{obs}, depends on $k_{T\Sigma}$, $[O_2]$, and the decay rate of the phthalocyanine triplet state in the absence of O_2, $\tau_T{}^{-1}$. according to the following expression:

$$k_{obs} = \tau_T{}^{-1} + k_{T\Sigma}[O_2] \qquad (1)$$

Quenching of the triplets of the Al, Ga, Ge, and Sn complexes by O_2 gives rise to biexponential-decay kinetics. This behavior

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(14) VanCott, T. C.; Rose, J. L.; Misener, G. C.; Williamson, B. E.; Schrimpf, A. E.; Boyle, M. E.; Schatz, P. N. *J. Phys. Chem.* **1989**, *93*, 2999–3011.

(15) (a) Dolphin, D.; James, B. R.; Murray, A. J.; Thornback, J. R. *Can. J. Chem.* **1980**, *58*, 1125–1132. (b) Doeff, M. M.; Sweigart, D. A. *Inorg. Chem.* **1981**, *20*, 1683–1687.

(16) Taube, R. *Pure Appl. Chem.* **1974**, *38*, 427–438.

(17) Our original assignment[4] of an emission maximum at 1190 nm to phosphorescence from $ZnPc(OBu)_8$ at 77 K is probably mistaken. We now believe that the peak is an artifact arising from a minimum in the transmission of the system near 1130 nm, similar to that responsible for the 1150-nm peak in Figure 3.

(18) The lack of phosphorescence from the octabutoxyphthalocyanines other than the Pd and Ru complexes contrasts to some extent with the behavior of unsubstituted phthalocyanines and even more so with the porphyrins,[5] but this trend is in line with the "energy gap law", which relates nonradiative decay rates to the energy gap between ground and excited states in molecules (see, e.g., ref 19 and references cited therein).

(19) Kober, E. M.; Capsar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722–3734.

is parallel to that observed previously with $H_2Pc(OBu)_8$[4] and metal naphthalocyanines.[7,20] It is due to reversible energy transfer between the phthalocyanines and O_2 and can be analyzed according to the model[7]

$$\begin{tikzcd}
\mathrm{Pc}\,(T_1) + O_2\,(^3\Sigma_g^-) \arrow[r, shift left, "k_{T\Sigma}"] \arrow[d, "k_T"] & \mathrm{Pc}\,(S_0) + O_2\,(^1\Delta_g) \arrow[l, shift left, "k_{\Delta G}"] \arrow[d, "k_\Delta"] \\
\mathrm{Pc}\,(S_0) & O_2\,(^3\Sigma_g^-)
\end{tikzcd}$$

where $k_{\Delta G}$ is the rate constant for energy transfer from O_2 ($^1\Delta_g$) to Pc (S_0), and k_T and k_Δ are the intrinsic rates of decay of Pc (T_1) and O_2 ($^1\Delta_g$), respectively. Supporting evidence for the existence of this equilibrium comes from the fact that monoexponential-decay kinetics for these complexes is observed after adding 2,5-dimethylfuran (0.08 M), a known quencher of O_2 ($^1\Delta_g$).[21,22] This adds a large first-order kinetic component to the decay of O_2 ($^1\Delta_g$), thereby overcoming the reverse step in the equilibrium.

In cases where triplet-decay kinetics are biexponential and where the forward and reverse reactions in the equilibrium are much more rapid than those depleting the equilibrium (i.e., $k_{T\Sigma}[O_2]$, $k_{\Delta G}[\mathrm{Pc}] \gg k_T, k_\Delta$), the measured rate of the early component (γ_1) has the analytical form given in eq 2.[7] The values of $k_{T\Sigma}$, which

$$\gamma_1 = k_{T\Sigma}[O_2] + k_{\Delta G}[\mathrm{Pc}] \qquad (2)$$

were evaluated from the dependence of either γ_1 (eq 2) or k_{obs} (eq 1) on $[O_2]$, range from 1.3×10^8 to 2.8×10^9 $M^{-1}\ s^{-1}$ (Table II).[23]

The singlet O_2 quantum yields in air-saturated benzene solutions, Φ_Δ, shown in Table II are equal to the values of Φ_T shown in Table I within experimental uncertainty except in the cases of $H_2Pc(OBu)_8$ and the Ru complex. It was not possible to determine Φ_Δ accurately for $H_2Pc(OBu)_8$. The triplet lifetime of $RuPc(OBu)_8(py)_2$ is so short that only 68% of the triplets is quenched in the air-saturated solution. When the solution is saturated with O_2 instead of air, 91% quenching is attained but the resulting value of Φ_Δ, 0.53, is still significantly less than that of Φ_T, 0.88. For the other phthalocyanines, 95% or greater triplet quenching is attained in air-saturated benzene.

The values of τ_Δ listed in Table II are the lifetimes of O_2 ($^1\Delta_g$) observed under the conditions used to obtain Φ_Δ. As is seen, these lifetimes range from less than 50 μs to over 500 μs. By comparison, the lifetime of O_2 ($^1\Delta_g$) in the standard solution of benzophenone is 730 μs in benzene-d_6 and 420 μs in benzene-d_6 containing 1% pyridine. Within the uncertainty of the measurements, the values of τ_Δ in the solutions of the metal-free, aluminum, gallium, germanium, and tin phthalocyanines are equal to the second lifetimes of the biexponential decays of the triplet state, which were obtained by transient absorbance measurements. This observation is in accordance with the kinetic model presented above since the lifetimes of O_2 ($^1\Delta_g$) and Pc (T_1) should be the same following establishment of the reversible energy-transfer equilibrium between these species.[7] Comparison of the values of τ_Δ for the the Zn, Ru, and Pd complexes to the values of τ_Δ for benzophenone indicates that these phthalocyanines quench O_2 ($^1\Delta_g$) with bimolecular rate constants that are in the range 1×10^7–5×10^7 $M^{-1}\ s^{-1}$.

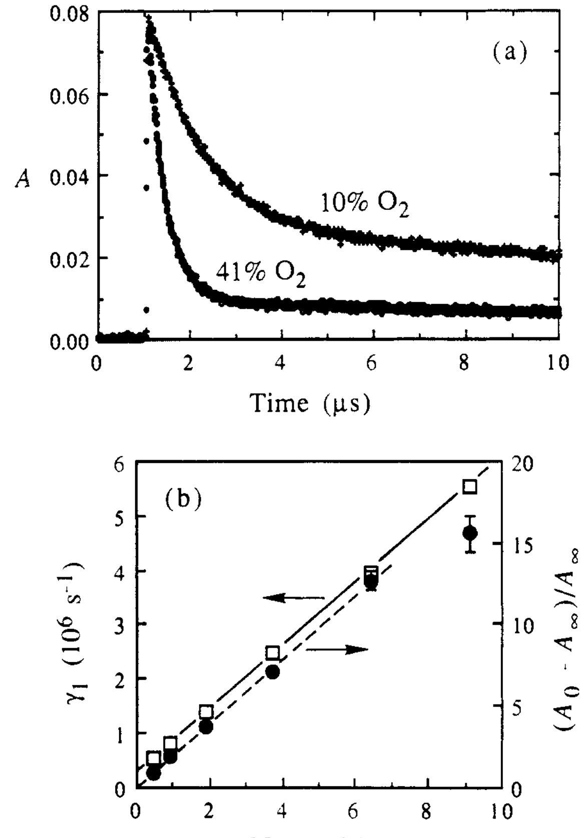

Figure 4. (a) Decay profiles of the triplet state of $AlPc(OBu)_8OSiEt_3$ in benzene solutions saturated with either 10–90 or 41–59 vol % O_2–N_2 mixtures. The triplet state was produced at time = 1 μs by pulsed laser excitation (10 ns, 355 nm) and was monitored by the net increase in absorbance at 590 nm. The phthalocyanine concentration was 22.5 μM. (b) Dependence on O_2 concentration of the parameters γ_1 (□) and $(A_0 - A_\infty)/A_\infty$ (●) for the triplet-state decay of $AlPc(OBu)_8OSiEt_3$. The parameters were obtained from transient absorbance changes exemplified by those shown in (a). The plots are in accord with eqs 2 and 3.

The energy-transfer reaction between $AlPc(OBu)_8OSiEt_3$ and O_2 was examined in detail in order to determine the equilibrium constant for the energy-transfer reaction, K_{eq} (which equals $k_{T\Sigma}/k_{\Delta G}$), and from this the triplet-state energy, E_T, for the Al complex. The concentration of O_2 was varied in these experiments while the concentration of phthalocyanine was kept constant. Representative time profiles of absorbance changes at 590 nm showing the decay of the phthalocyanine T_1 state at two concentrations of O_2 are reproduced in Figure 4a. These examples illustrate two effects on the triplet-state kinetics that result from increasing the concentration of O_2: (1) the rate constant of the early-decay component (γ_1) is increased and (2) the concentration of the triplet state at equilibrium, relative to its initial value, is decreased. The latter effect is expressed quantitatively[7] in eq 3,

$$(A_0 - A_\infty)/A_\infty = K_{eq}([O_2]/[\mathrm{Pc}]) \qquad (3)$$

where A_0 and A_∞ represent the total and equilibrium absorbance changes, extrapolated to $t = 0$, respectively. Figure 4b shows plots of the data according to eqs 2 and 3. Both plots give $K_{eq} = 0.044 \pm 0.001$. The value of $k_{\Delta G}$ obtained from these results is $(1.3 \pm 0.1) \times 10^{10}$ $M^{-1}\ s^{-1}$.

This value of K_{eq} can be used to estimate E_T of $AlPc(OBu)_8OSiEt_3$ since it is related to the difference between E_T and the energy required to promote O_2 ($^3\Sigma_g^-$) to its $^1\Delta_g$ state, E_Δ (22.54 kcal/mol). The relationship is given by eq 4, where $^1/_9$ is the

$$E_T - E_\Delta + RT \ln (^1/_9) = RT \ln K_{eq} \qquad (4)$$

spin-statistical factor that depresses the equilibrium-derived T_1 energy value relative to the spectroscopic value.[7,20] The value of E_T so derived is 21.99 kcal/mol. This value, together with the

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(20) Ford, W. E.; Rihter, B. D.; Rodgers, M. A. J.; Kenney, M. E. *J. Am. Chem. Soc.* **1989**, *111*, 2362–2363.

(21) Gorman, A. A.; Lovering, G.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1979**, *101*, 3050–3055.

(22) The triplet-state lifetime of the phthalocyanine in Ar-saturated solution, τ_T, is unaffected by the addition of 2,5-dimethylfuran.

(23) The kinetic constraints on the use of eq 2 were met with the Al, Ga, and Ge complexes ($k_T \leq 2 \times 10^4\ s^{-1}$) under the usual experimental conditions with benzene as solvent ($\tau_\Delta = 32$ μs, $k_\Delta = 3 \times 10^4\ s^{-1}$) because $[\mathrm{Pc}] \geq 10^{-5}$ M, $[O_2] \geq 10^{-3}$ M, $k_{T\Sigma} \geq 5 \times 10^8$ $M^{-1}\ s^{-1}$, and $k_{\Delta G} \approx 10^{10}$ $M^{-1}\ s^{-1}$. For the H_2 and Sn compounds, where the use of eq 2 was subject to doubt because of their relatively large k_T and small $k_{T\Sigma}$ values, the values of $k_{T\Sigma}$ were also determined by eq 1 after 2,5-dimethylfuran was added. The values of $k_{T\Sigma}$ evaluated either way were the same.

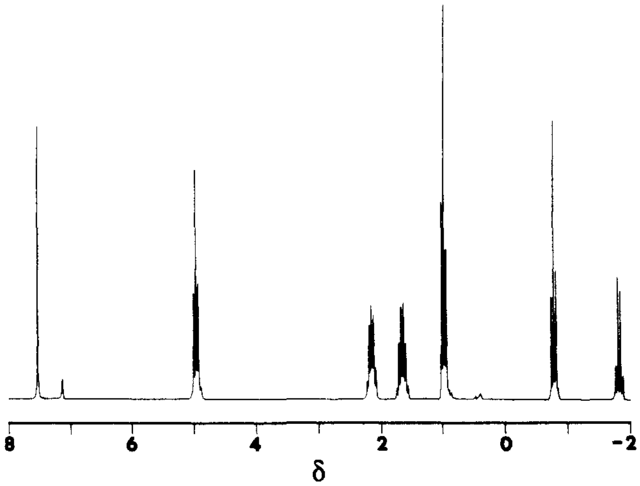

Figure 5. ^1H NMR spectrum of $GePc(OBu)_8(OSiEt_3)_2$ in benzene-d_6 at 50 °C.

singlet-state energy, E_S, estimated as 36.88 kcal/mol from spectroscopic data,[24] gives a value of 14.9 ± 0.1 kcal/mol as the S_1–T_1 energy gap, E_{ST}, in $AlPc(OBu)_8OSiEt_3$. This compares to our value of 15.6 ± 0.4 kcal/mol for E_{ST} in the 2,3-naphthalocyanines.[20]

Discussion

Syntheses. The syntheses of the metal octabutoxyphthalocyanines described are all metal-insertion syntheses in which a reactive-metal compound is used as the metal source. Syntheses of this type have been used commonly in the past to prepare phthalocyanines. For example, AlPcCl has been made from H_2Pc and $AlCl_3$,[25] and $GePcCl_2$ has been made from H_2Pc and $GeCl_4$.[26]

On the basis of the chemistry characteristic of the phthalocyanine ring and the metals involved and on the basis of infrared and NMR spectra obtained during the course of the work, the intermediates in the syntheses described appear to be those shown in Scheme I. The intermediate in the synthesis of the Ru complex, probably $RuPc(OBu)_8CO(py)$ as indicated, holds its CO very tenaciously. This is not surprising in view of the stability of the carbonyl(octaethylporphyrin)ruthenium Ru(OEP)CO(py)[27] and the ability of Ru^{II} to bond strongly to π-acid ligands.

Scheme I

$$H_2Pc(OBu)_8 + AlMe_3 \rightarrow AlPc(OBu)_8Me \xrightarrow{H_2O} AlPc(OBu)_8OH \xrightarrow{Et_3SiOH} AlPc(OBu)_8OSiEt_3$$

$$H_2Pc(OBu)_8 + GaCl_3 \rightarrow GaPc(OBu)_8Cl \xrightarrow{H_2O} GaPc(OBu)_8OH \xrightarrow{Et_3SiOH} GaPc(OBu)_8OSiEt_3$$

$$H_2Pc(OBu)_8 + GeCl_4 \rightarrow GePc(OBu)_8Cl_2 \xrightarrow{H_2O} GePc(OBu)_8(OH)_2 \xrightarrow{Et_3SiOH} GePc(OBu)_8(OSiEt_3)_2$$

$$H_2Pc(OBu)_8 + SnCl_4{\cdot}5H_2O \rightarrow SnPc(OBu)_8Cl_2 \xrightarrow{Et_3SiONa} SnPc(OBu)_8(OSiEt_3)_2$$

$$H_2Pc(OBu)_8 + PdCl_2(PPh_3)_2 \rightarrow PdPc(OBu)_8$$

$$H_2Pc(OBu)_8 + Ru_3(CO)_{12} + py \rightarrow RuPc(OBu)_8CO(py) \xrightarrow[h\nu]{py} RuPc(OBu)_8(py)_2$$

NMR Spectra. In the NMR spectrum of $GePc(OBu)_8(OSiEt_3)_2$, Figure 5, the α- and β-methylene resonances of the butoxy groups are in the 4.9–5.1 and 2.1–2.2 ppm ranges. In the spectra of the other compounds studied, the α- and β-methylene resonances of the butoxy groups are in the same ranges. This suggests that for all these compounds the shielding of the α- and β-protons arising from ring-current effects is similar. Because the Ge and Sn complexes have trans siloxy groups and thus cannot be appreciably associated in benzene-d_6, it appears that none of the other octabutoxyphthalocyanines are substantially associated in benzene-d_6 under the conditions used.

As is seen, the methyl and methylene resonances of the ethyl groups of the Al and Ga complexes are at appreciably lower field than those of the Ge and Sn complexes. This indicates that the ethyl groups of the Al and Ga complexes are less shielded by ring-current effects and, thus, that the siloxy groups in these compounds are most distant from the ring plane and that the metals in them are out of the ring plane.

The α-methylene multiplets of the butoxy groups of the Al and Ga compounds are more complex than those of the Ge and Sn compounds. Similarly, though to a lesser extent, the β- and γ-multiplets of the Al and Ga compounds are more complex than those of the Ge and Sn compounds. This indicates that the protons of the methylenes are subject to unequal average shielding. This is attributed to structural differences on the two sides of the ring. A similar interpretation has been given for the complex asymmetric methylene multiplet of the octaethylporphyrin $Tl(OEP)OH(H_2O)$.[28]

As already noted, the α- and β-methylene multiplets of the Pd and Ru complexes are in positions similar to those of the other compounds. In addition, like those of the other octabutoxyphthalocyanines, they are well resolved. This shows that the Pd and Ru do not have unpaired electrons. The absence of unpaired electrons in the Pd and Ru complexes can be attributed to the electron configurations of the metals (d^8 and d^6), their coordination arrangements (square and octahedral), and the strengths of the ligand fields provided by the ring and pyridine.

The position of the ring protons of $RuPc(OBu)_8(py)_2$ is significantly below the positions of the ring protons of the other compounds. Because of this, it appears that the Ru interacts with the ring to a substantially different and probably greater extent than the metals of the other compounds do. A greater positive overlap between the metal d-orbitals and the ring π-orbitals probably underlies this difference.[5]

Finally, the resonance of the central protons of the metal-free compound is at much lower field than the positions of the central protons of H_2Pc(2- and/or 3-$CMe_3)_4$ and H_2Pc(2- and/or 3-$SiMe_3)_4$, −2.0 and −2.7.[29] This difference is attributed to the differences in the inductive effects of the peripheral groups.

Photoproperties. We limited the metals chosen for this study to those whose porphyrin or phthalocyanine complexes are known to have relatively long triplet-state lifetimes.[5] This eliminated from consideration complexes of transition-metal ions with d-electron configurations having unpaired electrons.

Comparisons of the photoproperties of the metal octabutoxyphthalocyanines can be made between elements within both groups and periods in the periodic table in order to highlight the effects of atomic number and oxidation state. One effect that is evident from the data is the heavy-atom effect on triplet yield and lifetime (Table I). This effect is due to increases in the rates of intersystem crossing between the singlet and triplet states as a result of enhanced spin–orbit coupling and is well-known for porphyrins and phthalocyanines.[5] Also of interest is that, within the group IIIA complexes (Al and Ga) and the IVA complexes (Ge and Sn), the singlet-state energy decreases with increasing atomic number. Within the first long-period complexes (Zn, Ga, and Ge) and the second long-period complexes (Ru, Pd, and Sn), the general trend is an increase in the triplet-state lifetime and a decrease in the

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[24] The singlet-state energy, E_S, is taken to be midway between the energies of the 0,0 transitions in the absorption and fluorescence spectra: $E_S = {}^1/_2(E_{max}{}^{abs} + E_{max}{}^{fl})$.

[25] Barrett, P. A.; Dent, C. E.; Linstead, R. P. *J. Chem. Soc.* **1936**, 1719–1736.

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[29] Hanack, M.; Metz, J.; Pawlowski, G. *Chem. Ber.* **1982**, *115*, 2836–2853.

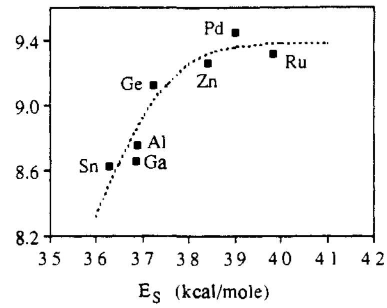

Figure 6. Semilogarithmic plot of the dependence of the bimolecular rate constant, $k_{T\Sigma}$, for triplet-state quenching of metal octabutoxyphthalocyanines by O_2 on the singlet-state energy of the phthalocyanine, E_S. The dotted line is the least-squares best fit of the experimental data to the modified Sandros equation (eq 5) with E_{ST} = 14.9 and $^1/_9k_{diff}$ = 2.4 × 10^9 M^{-1} s^{-1}.

singlet-state energy with increasing oxidation state.[30]

As pointed out above, the NMR results indicate that a substantially greater metal–phthalocyanine interaction occurs in $RuPc(OBu)_8(py)_2$ than in the other compounds. This interaction is reflected in the blue-shifted absorption maxima of the Ru complex relative to the others. The unusually large Stokes shift in $RuPc(OBu)_8(py)_2$ suggests that the geometry of the S_1 state of the complex is different from the geometry of the ground state. Since the trans axial ligands of some ruthenium phthalocyanines having axial ligands are photolabile,[15a] the large Stokes shift in $RuPc(OBu)_8(py)_2$ may reflect some photoprocess involving the pyridine groups.

The triplet-state energies, E_T, of the ruthenium and palladium octabutoxyphthalocyanines, which are obtained from the phosphorescence measurements, are 31.4 and 26.0 kcal/mol, respectively. The corresponding S_1–T_1 energy gap, E_{ST}, is 8.4 kcal/mol in the Ru complex and 13.0 kcal/mol in the Pd complex, which are significantly less than E_{ST} in the Al complex (14.9 kcal/mol) and the other main-group complexes (vide infra). Some estimation of E_{ST} in the series of main-group complexes can be obtained from the dependence of $k_{T\Sigma}$ on the singlet-state energy, E_S, by using a modified version of the Sandros equation (eq 5), as was done

$$k_{T\Sigma} = (^1/_9k_{diff})(1/(1 + \exp(-(E_S - E_{ST} - E_\Delta)/RT))) \quad (5)$$

earlier with naphthalocyanines.[20] The relationship in eq 5 assumes that E_{ST} does not vary significantly within the series. Figure 6 shows the plot of log $k_{T\Sigma}$ versus E_S, which includes all seven of the metal complexes. A nonlinear least-squares fit[31] of the experimental values of $k_{T\Sigma}$ and E_S to eq 5 for the main-group elements alone (Al, Zn, Ga, Ge, and Sn) gives estimates for $^1/_9k_{diff}$ and E_{ST} of (2.2 ± 0.4) × 10^9 M^{-1} s^{-1} and 14.7 ± 0.3 kcal/mol, respectively. The least-squares fit obtained for all seven data points gives estimates for $^1/_9$ k_{diff} and E_{ST} of (2.4 ± 0.3) × 10^9 M^{-1} s^{-1} and 14.9 ± 0.3 kcal/mol, respectively. The line drawn in Figure 6 is the solution to eq 5 with the latter parameters. The value of $^1/_9k_{diff}$ is close to the average of the values of $k_{T\Sigma}$ for the Ru and Pd complexes, 2.5 × 10^9 M^{-1} s^{-1}. As is seen, the data suggest that the assumption that E_{ST} does not vary significantly within the main-group metal complexes is valid. The value of E_{ST} obtained, 14.9 ± 0.3 kcal/mol, agrees with the value determined from K_{eq} for $AlPc(OBu)_8OSiEt_3$. The point for $H_2Pc(OBu)_8$ (not shown) falls well below the curve for the metal complexes, indicating that E_{ST} for this compound is significantly greater than 14.9 kcal/mol.

Conclusions

The octabutoxyphthalocyanines are a chemically stable group of phthalocyanines that can be made by the procedures ordinarily used to make phthalocyanines. They have intense absorptions in the far-red that are intermediate in position between those of the phthalocyanines and those of the naphthalocyanines. It appears that their triplet-state yields are also intermediate, being higher than those of naphthalocyanines but lower than those of phthalocyanines. The triplet-state energies of the complexes of the main-group elements are about 0.5 kcal/mol greater than those of naphthalocyanines having similar absorption maxima because they have a smaller S_1–T_1 energy gap. This is a significant difference when these compounds are being considered as photosensitizers for O_2 ($^1\Delta_g$) because of the proximity of their triplet-state energies to that of O_2 ($^1\Delta_g$). Experiments are in progress to evaluate the pharmacokinetic and phototherapeutic effectiveness of selected members of this group of compounds.

Acknowledgment. Support for this project came in part from NIH Grant CA 46281 and from the Center for Photochemical Sciences at Bowling Green State University. Mass spectra determinations were performed by the Midwest Center for Mass Spectroscopy at Lincoln, NE, a National Science Foundation Regional Instrumentation Facility (Grant CHE 8620177).

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(30) These trends are attributed to the changes in oxidation state rather than atomic number because the latter are relatively small and because the observed increases in triplet-state lifetimes are opposite to the behavior expected from the heavy-atom effect.

(31) The nonlinear regression analysis was performed with a microcomputer using the Levenberg–Marquardt nonlinear least-squares algorithm (NCSS software).