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Mixed-Ligand Palladium(II) and Platinum(II) Complexes—Photosensitizers of $^1O_2$ Production and Chemical Quenchers of $^1O_2$

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[M(nn)(dhn)] (where M is Pd(II) or Pt(II), nn is 2,2′-bipyridine, 1,10-phenanthroline, 2,2′-biquinoline, or 4,7-diphenyl-1,10-phenanthroline, and dhn is dianion of 2,3-naphthalenediol) photooxidizes the 2,2,6,6-tetramethyl-4-piperidinol in *N,N*-dimethylformamide via $^1O_2$ when irradiated with light of wave-lengths of 420 to 800 nm in presence of molecular oxygen. The presence of $^1O_2$ as an intermediate is confirmed by quenching studies using bis(dibutyldithiocarbamato)nickel(II) and 20% water in DMF. The relative efficiency of $^1O_2$ production sensitized by the above complexes depends on nature of metal, ligand, and geometry of the complexes. However, [Pd(bpy)(dmt)] and [Pd(phen)(dmt)] undergo photooxidation via $^1O_2$ when sensitized by hematoporphyrin IX and its metal derivatives on photolysis under similar conditions. The relative efficiency of $^1O_2$ production depends on the nature of metal in porphyrin.

Photolysis of chloroform solution of [Pt(bpy)(dmt)] (where bpy is 2,2′-bipyridine and dmt is dianion of 3,4-toluenedithiol) at 577 nm in ligand-to-ligand charge-transfer (LLCT) transition region results in an electron transfer from the complex to chloroform. A ligand-centered radical (probably the easily oxidized dmt) $[Pt(bpy)(dmt)]^+$ decomposes into unidentified products.[1)] Photolysis of [Ni(phen)(dmde)] (where phen is 1,10-phenanthroline and dmde is dianion of cis-1,2-diphenylethylene-1,2-dithiol) in $CHCl_3$ in LLCT transition region has also promoted analogous photooxidation.[2)] Similar mixed-ligand complexes of palladium(II) and platinum(II) complexes of formula [M(nn)(xx)] (where M is Pd(II) or Pt(II), nn is 2,2′-bipyridine or 1,10-phenanthroline, and xx is dianion of catechol, 4-*t*-butylcatechol, 3,4-dimercaptotoluene or thiosalicylic acid (tsa)) in *N,N*-dimethylformamide (DMF) have been used to photosensitize the singlet molecular oxygen ($^1O_2$) production when irradiated in their LLCT transition region between 400 and 700 nm in presence of molecular oxygen.[3,4)] However, [Pt(nn)(dmt)] and [Pt(nn)(tsa)] undergo self-sensitized photooxidation via $^1O_2$,[4—6)] and [Ni(nn)(dmt)] as physical quenchers of $^1O_2$.[7)] In this paper we report the photo-sensitizing ability of [M(nn)(dhn)] (where nn is 2,2′-bipyridine, 1,10-phenanthroline, 2,2′-biquinoline (biq), or 4,7-diphenyl-1,10-phenanthroline (dpp) and dhn is dianion of 2,3-naphthalenediol) in DMF to produce $^1O_2$, and the chemical quenching of $^1O_2$ by [Pd(bpy)(dmt)] and [Pd(phen)(dmt)] using hematoporphyrin IX and its metal derivatives as photosensitizers.

Experimental

Materials: [Pd(nn)(dmt)] and [M(nn)(dhn)] were prepared and characterized as described elsewhere.[4,8)] Bis(dibutyldithiocarbamato)nickel(II), $[Ni(dbdc)_2]$, was prepared by the reported procedure.[9)] Nickel(II), palladium(II), and platinum(II) complexes of hematoporphyrin IX were prepared and purified by the literature methods.[10,11)] Chemicals used were of reagent grade and purified before use. The reagent grade solvents were purified before use by the standard procedures.[12)]

Physical Measurements: Phosphorescence measurements were made with a SPEX 1934C phosphorimeter with RCA C13034 photomultiplier attachment having facility to give corrected emission spectra. Metal complexes dissolved in ethanol (1×10^{-6} M, $1M=1$ mol dm^{-3}) were frozen in liquid nitrogen (77 K) in a 10 mm quartz cuvette and the spectra of the frozen solutions were recorded using different wavelengths of excitation. Other physical methods used were described elsewhere.[3,8)]

General Irradiation Procedures: The irradiation of molecular oxygen saturated DMF solutions of metal complexes were carried out in a triple jacket merry-go-round apparatus as described earlier,[3)] except 250 W tungsten halogen lamp was used in place of 150 W.

The photochemical measurements were also carried out by following modified method of Diamond and coworkers[13)] as described elsewhere.[6)]

Results and Discussion

Phosphorescence Spectra of [M(bpy)(dhn)]. The phosphorescence spectra of [M(bpy](dhn)] (where M is Pd(II) or Pt(II)) in ethanol glass at 77 K on excitations at their different absorption maxima show a broad band at about 600 nm. [Pd(bpy)(dhn)] on excitation at 457, 337, and 297 nm gives a phosphorescence band at 607 nm. [Pt(bpy)(dhn)] exhibits a band at 601 nm on excitation at 478, 338, and 296 nm as shown in Fig. 1. The phosphorescence band at about 600 nm in the above complexes is due to the longest wavelength LLCT transition as reported earlier for [Pt(bpy)(dmt)].[1)] These data suggest that the triplet state of LLCT transition is expected to be involved in the following photooxidation reactions.

Photooxidation of 2,2,6,6-Tetramethyl-4-piperidinol (XH) and Its Quenching Studies: Molecular oxygen saturated DMF solution of [M(nn)(dhn)] (200 μM) in presence of XH (10 mM) was irradiated with light of wavelengths from 420 to 800 nm for different irradi-

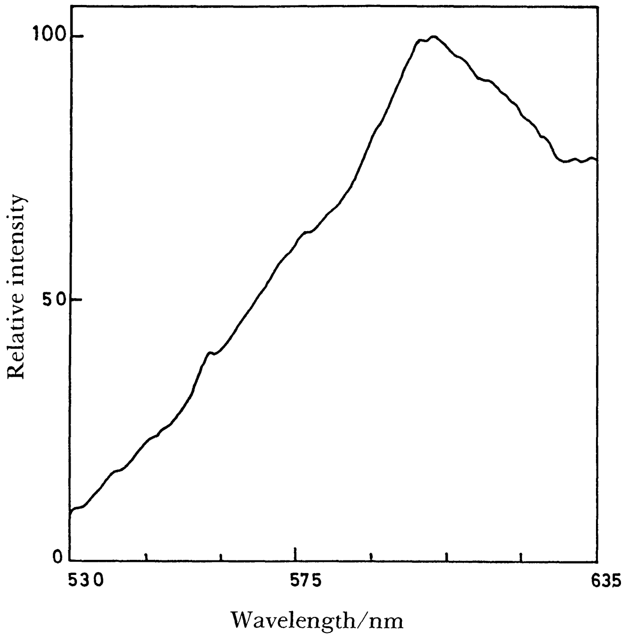

Fig. 1. A phosphorescence spectrum of [Pt(bpy)(dhn)] in ethanol glass at 77 K.

ation times in a merry-go-round apparatus. The $^1O_2$ molecules formed combine with XH molecules to produce 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy free radicals (XO) which is measured by EPR method.[3)] There is a linear relationship between the amount of XO free radicals formed and the irradiation times for different [M(nn)(dhn)] as shown in Fig. 2. It is supposed that [Pd(dpp)(dhn)] yields the maximum amount of $^1O_2$ as it has the highest slope, whereas [Pd(biq)(dhn)] yields the lowest amount of $^1O_2$ as it exhibits the smallest slope. The relative yields of $^1O_2$ production referred to [Pd(dpp)(dhn)] are given in Table 1. The values of relative efficiency calculated after correcting for the amounts of light absorbed using relative integrated areas under the absorption curves. After correcting the wavelength distribution of the lamp, they are given in Table 1. The relative efficiencies follow the order: [Pd(dpp](dhn)]>[Pt(dpp)(dhn)]>[Pt(bpy)(dhn)]>[Pt(phen)(dhn)]>[Pt(biq)(dhn)]>[Pd(biq)(dhn)]≈[Pd(bpy)(dhn)]≈[Pd(phen)(dhn)].

The formation of nitroxide free radicals was not observed when the solution of [M(nn)(dhn)] or 2,2,6,6-tetramethyl-4-piperidinol was kept in dark or irradiation in presence of molecular nitrogen. There was also no change in the position and intensity of absorption bands between 420 and 800 nm of [M(nn)(dhn)] in molecular oxygen saturated DMF after irradiations for two hours. The photooxidation of XH sensitized by [M(nn)(dhn)] was studied in 20% water-DMF. In these experiments the molecular oxygen saturated solutions of [Pd(dpp)(dhn)] (200 μM) in presence of XH (10 mM) in 20% water-DMF and in 100% DMF respectively were irradiated with light of wavelengths from 420 to 800 nm for different irradiation times. The plots of amount of XO free radicals against irradiation time are given in Fig. 3. The slope decreases in 20% water-DMF. The shortening of lifetime (τ) of $^1O_2$ can be affected by using mixed solvents such as 20% water in DMF (τ of $^1O_2$ in pure water is 2 μs and τ of $^1O_2$ in pure DMF is 7.1 μs).[14)] There is an appreciable decrease in slope in 20% water in DMF than in pure DMF as shown in Fig. 3.

The quenching of photooxidation of 2,2,6,6-tetramethyl-4-piperidinol sensitized by [M(nn)(dhn)] was studied using bis(dibutyldithiocarbamato)nickel(II) as physical quenchers of $^1O_2$. In these quenching experiments the molecular oxygen saturated solutions containing [Pt(phen)(dhn)] (5×10^{-5} M), bis(dibutyldithiocarbamato)nickel(II) (10^{-5} M or 10^{-6} M) and five different concentrations of XH (varying from 1×10^{-2} to 2×10^{-3} M) were irradiated using light of wavelengths from 420 to 800 nm for 1 h. The amount of XO free radicals produced was measured by EPR method.[3)] The 1/[XO] was plotted against 1/[XH] for two concentrations of the nickel(II) complex. Two linear plots with their intercepts meeting at a

Table 1. Relative Yields and Efficiencies of [M(nn)(dhn)] for Sensitizing the Generation of $^1O_2$[a)]

Complex	Relative yield of $^1O_2$ production referred to [Pd(dpp)(dhn)]	Relative efficiency of $^1O_2$ production referred to [Pd(dpp)(dhn)]
[Pd(dpp)(dhn)]	1.00	1.00
[Pt(dpp)(dhn)]	0.27	0.63
[Pt(bpy)(dhn)]	0.22	0.15
[Pt(phen)(dhn)]	0.30	0.13
[Pt(biq)(dhn)]	0.12	0.07
[Pd(biq)(dhn)]	0.04	0.05
[Pd(bpy)(dhn)]	0.05	0.04
[Pd(phen)(dhn)]	0.08	0.02

a) Relative integrated areas under absorption curves between 420 and 800 nm of [Pd(dpp)(dhn)], [Pt(dpp)(dhn)], [Pt(bpy)(dhn)], [Pt(phen)(dhn)], [Pt(biq)(dhn)], [Pd(biq)(dhn)], [Pd(bpy)(dhn)], and [Pd(phen)(dhn)] for 5×10^{-5} M are in the ratio 1.00 : 0.43 : 1.49 : 2.39 : 1.71 : 0.89 : 1.11 : 3.50, respectively.

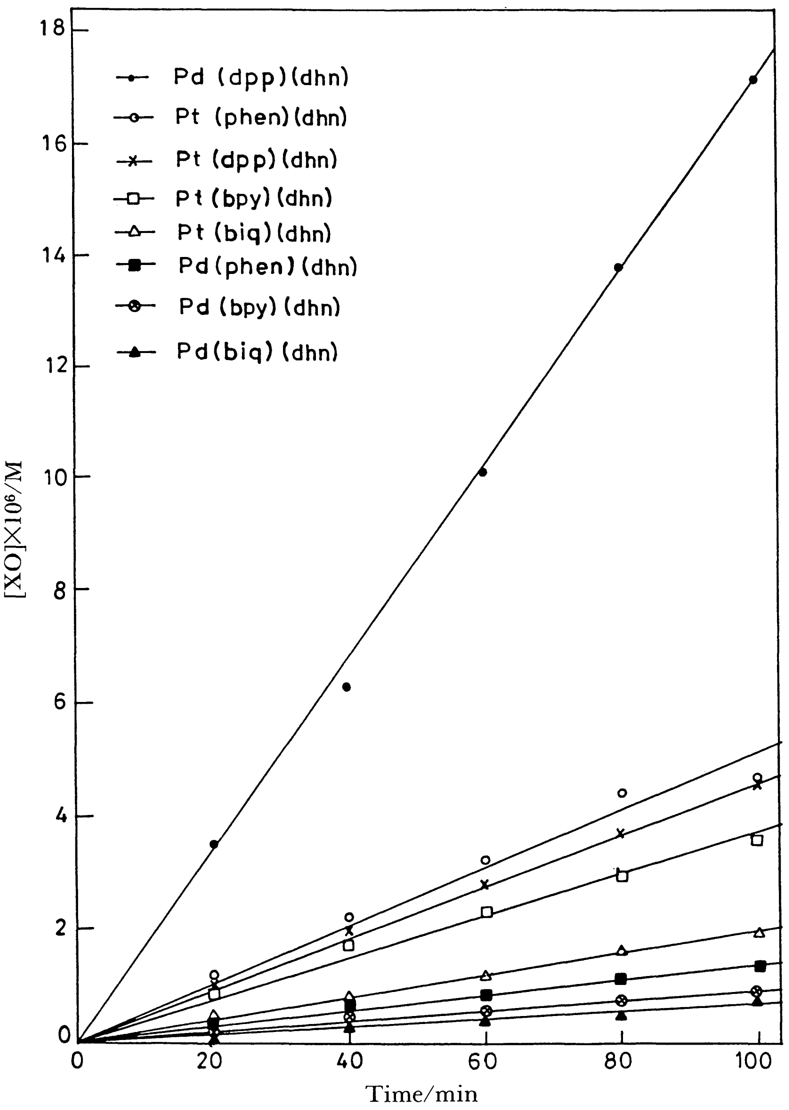

Fig. 2. Plots of XO free radical concentration versus irradiation time of solutions of [M(nn)(dhn)] (2×10^{-4} M) in presence of 2,2,6,6-tetramethyl-4-piperidinol (1×10^{-2} M) in DMF.

same point on the y-axis were obtained and they are given in Fig. 4. The relative amount of light absorbed by the nickel(II) complex in the wavelength range of 420 to 800 nm, at 10^{-5} or 10^{-6} M, is less than 0.1% as compared to [Pt(phen)(dhn)] and, therefore, there is no competition for light absorption between the sensitizer and the quencher.

The above results suggest that the photooxidation of 2,2,6,6-tetramethyl-4-piperidinol sensitized by [M(nn)(dhn)] involves the $^1O_2$ as an intermediate and the triplet state of LLCT transition in [M(nn)(dhn)] is responsible for the production of the $^1O_2$ by energy transfer.[3] The following Scheme 1 suggests the mechanism for the above reaction.[3] (S is one of the [M(nn)(dhn)] as photosensitizer, ^1S and ^3S are its first excited singlet and triplet states respectively, $h\nu$ is the energy of a photon, ISC is the inter system crossing, ET is the energy transfer, k_d is the rate constant of quenching of $^1O_2$ by DMF molecules, k_r is the rate constant of chemical quenching of $^1O_2$ by XH to produce XO, and k_q is the physical quenching of $^1O_2$ by the bis(dibutyldithiocarbamate)nickel(II) (Q).

$$\mathrm{S} \xrightarrow{h\nu} {}^1\mathrm{S} \qquad \text{(i)}$$

$$^1\mathrm{S} \xrightarrow{\mathrm{ISC}} {}^3\mathrm{S} \qquad \text{(ii)}$$

$$^3\mathrm{S} + {}^3\mathrm{O}_2 \xrightarrow{\mathrm{ET}} {}^1\mathrm{S} + {}^1\mathrm{O}_2 \qquad \text{(iii)}$$

$$^1\mathrm{O}_2 \xrightarrow{k_d} {}^3\mathrm{O}_2 \qquad \text{(iv)}$$

$$^1\mathrm{O}_2 + \mathrm{XH} \xrightarrow{k_r} \mathrm{XO} \qquad \text{(v)}$$

$$^1\mathrm{O}_2 + \mathrm{Q} \xrightarrow{k_q} {}^3\mathrm{O}_2 + \mathrm{Q} \qquad \text{(vi)}$$

Scheme 1.

On the assumption of above mechanism (see Scheme

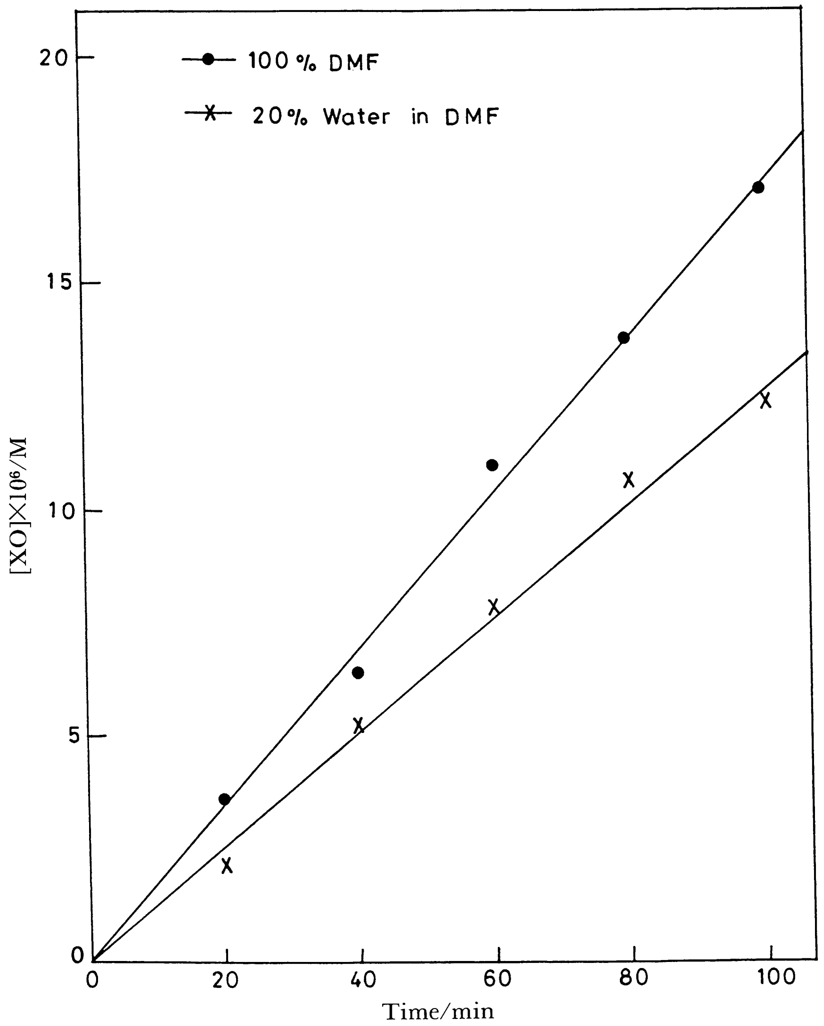

Fig. 3. Plots of XO free radical concentration versus irradiation time of [Pd(dpp)(dhn)] (2×10^{-4} M) and 2,2,6,6-tetramethyl-4-piperidinol (1×10^{-2} M) in DMF and 20% H_2O in DMF.

1) the rate of formation of XO free radicals by oxidation of XH with $^1O_2$ using steady state approximation, can be given by Eq. 1.[3] (I_{abs} is the intensity of

$$\frac{d[XO]}{dt} = I_{abs}\,\phi_{^1O_2}\frac{k_r[XH]}{k_r[XH]+k_d}, \tag{1}$$

irradiation and $\phi_{^1O_2}$ is the quantum yield of $^1O_2$ production). If I_{abs} is not constant for [M(nn)(dhn)] and k_d, k_r, and [XH] are kept constant, the slope of the plot of the amount of nitroxide radicals produced versus irradiation time is related to $I_{abs}\phi_{^1O_2}$ (called yield of $^1O_2$ production). The slopes of linear plots of amount of nitroxide radicals produced versus irradiation time for [M(nn)(dhn)] are shown in Fig. 2. The relative yields of $^1O_2$ production for [M(nn)(dhn)] referred to [Pd(dpp)(dhn)] were obtained from the slopes of Fig. 2 and they are given in Table 1.

On correcting for the relative amounts of light absorbed by [M(nn)(dhn)] using Eq. 2, the relative

$$\frac{(\phi_{^1O_2})_2}{(\phi_{^1O_2})_1} = \frac{(\text{slope})_2}{(\text{slope})_1}\times\frac{(I_{abs})_1}{(I_{abs})_2}, \tag{2}$$

efficiencies of $^1O_2$ production for [M(nn)(dhn)] referred to [Pd(dpp)(dhn)] were obtained. These values are also given in the last column of Table 1 and the order follows as given above. The efficiency order seems to depend on nature of metal ion, nature of α-diimine ligand, and the energy of ligand-field A_2 state with respect to the lowest triplet state (π,π^*).[3,15]

If the last step in parentheses of the above mechanism is included, Eq. 3 is obtained as

$$\frac{1}{[XO]} = \frac{1}{[^1O_2]} + \frac{k_q[Q]+k_d}{k_r}\times\frac{1}{[^1O_2]}\times\frac{1}{[XO]}. \tag{3}$$

On plotting 1/[XO] against 1/[XH] (see Fig. 4) a linear plot is obtained with the slope$=1/[^1O_2]\times(k_q[Q]+k_d)/k_r$ and the intercept$=1/[^1O_2]$. Knowing k_d (1.4×10^5 s^{-1} in DMF),[14] k_r (2.45×10^7 M^{-1}s^{-1})[3,16] and concentrations of Q (1×10^{-5} M or 1×10^{-6} M), slope and inter-

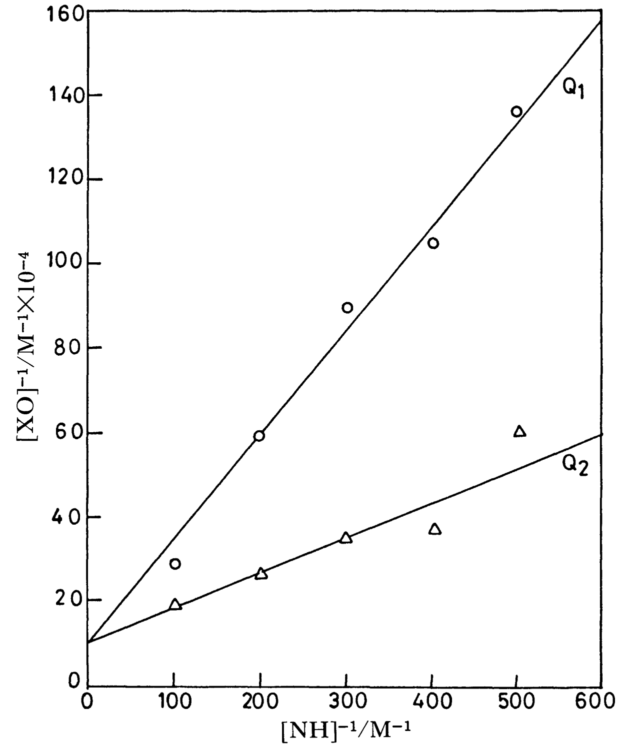

Fig. 4. Plots of reciprocal of XO free radical concentration versus reciprocal of 2,2,6,6-tetramethyl-4-piperidinol in presence of bis(dibutyldithiocarbamato)nickel(II) (10^{-5} M (Q_1) and 10^{-6} M (Q_2)) using [Pt(phen)(dhn)] (5×10^{-5} M) as a photosensitizer.

cept (from above mentioned plot), the k_q can be obtained. The k_q values obtained for bis(dibutyldithiocarbamato)nickel(II) ([Ni(dbdc)$_2$]) at concentrations of 1.0×10^{-5} and 1×10^{-6} M are 4.6×10^{10} and 6.3×10^{10} M^{-1} s^{-1}, respectively. Thus, the average value of k_q is 5.5×10^{5} M^{-1} s^{-1}, which is higher than the reported value.[14] For the two plots as given in Fig. 4, the intercepts meet at a point on the y-axis for 1×10^{-5} M and 1×10^{-6} M [Ni(dbdc)$_2$]. However, the slope increases with increase in concentrations of [Ni(dbdc)$_2$]. This suggests that the physical quenching of $^1O_2$ by the [Ni(dbdc)$_2$] is involved and it rules out any quenching of excited sensitizer [Pt(phen)(dhn)].[14]

Photooxidation of [Pd(nn)(dmt)] Sensitized by Hematoporphyrin IX and Its Metal Derivatives: A solution of [Pd(bpy)(dmt)] or [Pd(phen)(dmt)] (5×10^{-4} M) and porphyrin (5×10^{-5} M) in DMF was bubbled with DMF saturated molecular oxygen for 15 min. This solution was taken in a stoppered quartz cuvette of 1 cm path length and was then irradiated for different intervals of time by the light source directed first through the filter and then through an acrylic cylinder.[13] The course of the photolysis of [Pd(bpy)(dmt)] or [Pd(phen)(dmt)] (5×10^{-4} M) sensitized by a free porphyrin or a metal porphyrin (5×10^{-5} M), after irradiating with light of wavelengths between 455 and 800 at different irradiation time (0 to 10 min), was followed by the difference absorption spectroscopy using same concentration of free porphyrin or metal porphyrin (5×10^{-5} M) in a reference cuvette in the visible region using a Shimadzu UV-260 spectrophotometer. The absorbance (A) of the [Pd(bpy)(dmt)] or [Pd(phen)(dmt)] at different time of photolysis was calculated by substracting the reduction of absorbance at 498 or 500 nm obtained by difference absorption spectroscopy from the initial absorbance of the [Pd(bpy)(dmt)] or [Pd(phen)(dmt)] (5×10^{-4} M). The reduction of absorbance of the palladium(II) complex (5×10^{-4} M) due to photolysis for 10 min irradiation was less than 1% of total absorbance of a free porphyrin or a metal porphyrin (5×10^{-5} M).

The plots of logarithm A of [Pd(bpy)(dmt)] at 498 nm versus different irradiation time of 0 to 10 min for free hematoporphyrin IX and its metal derivatives are shown in Fig. 5. These linear plots have different slopes and the ratio of these slopes is related to relative yields of $^1O_2$ production for different metal hematoporphyrin IX as compared to free hematoporphyrin IX (with its normalized value taken as 1) and these ratios are given in Table 2.

The relative efficiencies of $^1O_2$ production by the

Table 2. Relative Yields and Efficiencies of Hematoporphyrin IX and Its Metal Derivatives to Sensitize the Generation of $^1O_2$

Porphyrin	[Pd(bpy)(dmt)] as chemical quencher		[Pd(phen)(dmt)] as chemical quencher		2,2,6,6-Tetramethytl-4-piperidiol as chemical quencher	
	Relative yield of $^1O_2$ production referred to H_2HP	Relative efficiencies of $^1O_2$ production referred to H_2HP[a]	Relative yield of $^1O_2$ production referred to H_2HP	Relative efficiencies of $^1O_2$ production referred to H_2HP[a]	Relative yield of $^1O_2$ production referred to H_2HP	Relative efficiencies of $^1O_2$ production referred to H_2HP[a]
H_2HP	1.00	1.00	1.00	1.00	1.00	1.00
PdHP	0.76	0.63	0.72	0.60	0.78	0.65
PtHP	0.48	0.40	0.50	0.42	0.51	0.43
NiHP	0.03	0.03	0.03	0.03	0.03	0.03

a) Relative integrated areas under absorption curves between 420 and 800 nm of hematoporphyrin IX (H_2HP), PdHP, PtHP, NiHP for 1×10^{-5} M after correcting for amounts of light absorbed are in ratio of 1.0 : 1.2 : 1.2 : 1.1, respectively.

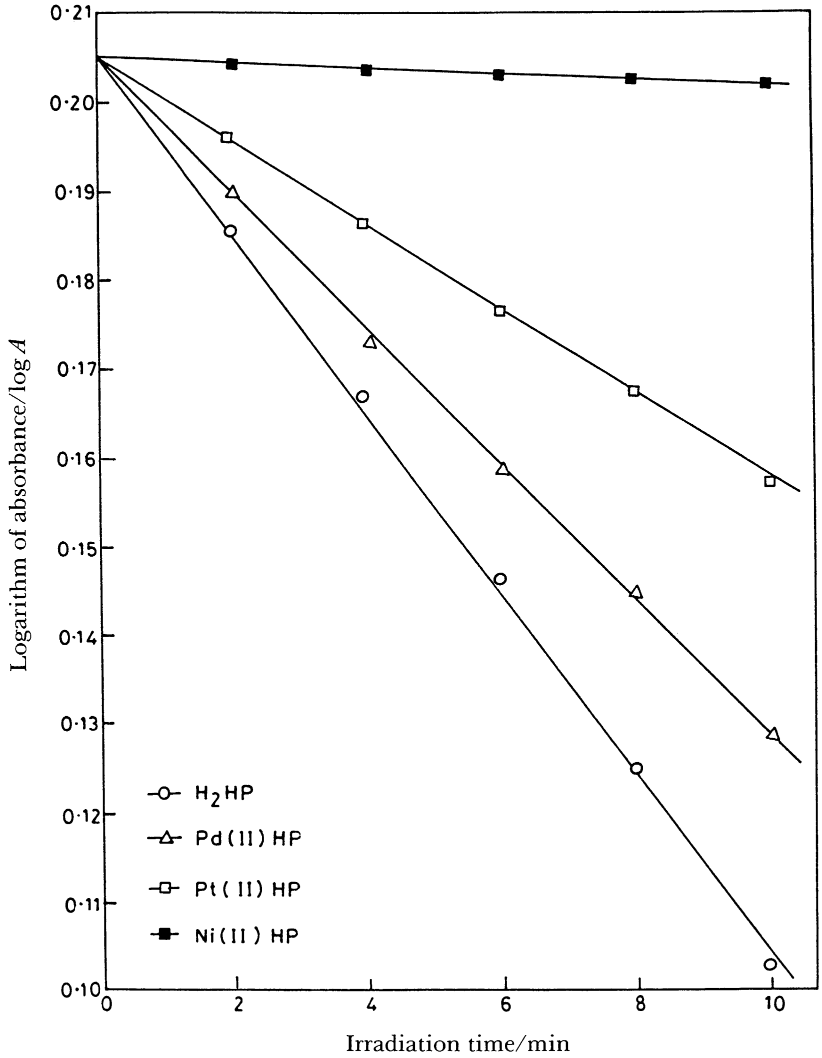

Fig. 5. Plots of log$A$ versus irradiation time (A is absorbance at 498 nm of [Pd(bpy)(dmt)] (5×10^{-4} M) in DMF containing porphyrins (5×10^{-4} M)).

different metal hematoporphyrin IX referred to free hematoporphyrin IX after making corrections for the relative amounts of light absorbed by them have been compared and the values are also given in Table 2. The relative yields or the relative efficiencies of $^1O_2$ production by above porphyrins using [Pd(bpy)(dmt)] as a chemical quencher (see Table 2) follow the order: $H_2HP>PdHP>PtHP\gg NiHP$. Similar plots were obtained using [Pd(phen)(dmt)] as a chemical quencher. In this case the relative yields or relative efficiencies of $^1O_2$ production by porphyrins (see Table 2) follow the same order: $H_2HP>PdHP>PtHP\gg NiHP$.

Hematoporphyrin IX and its metal derivatives are good photosensitizers of $^1O_2$ production[17] and this $^1O_2$ oxidizes the chemical quenchers [Pd(bpy)(dmt)] and [Pd(phen)(dmt)].[18] The mechanism suggested earlier to explain the photooxidation of [Pd(bpy)(dmt)] and [Pd(phen)(dmt)] sensitized by hematoporphyrin IX is also acceptable when Ni(II), Pd(II), and Pt(II) hematoporphyrin IX complexes were used as photosensitizers in place of hematoporphyrin IX in the above photooxidation reactions. The steps involved in these photooxidation reactions are same as given for Scheme 1 (see above) except that S is one of the porphyrins acting as sensitizer, and XH and Q are replaced by Q′ (where Q′ is [Pd(bpy)(dmt)] or [Pd(phen)(dmt)] because the Q′ behaves both as chemical and physical quencher (see steps V and VI in Scheme 1). In the light of this mechanism the log[Q′] can be given by the following relationship.[18,19]

$$\log[Q'] = -kt + c \quad (\text{if } k_d \gg (k_q + k_r)[Q'], \tag{4}$$

and

$$k = I_{abs}\phi_{^1O_2}\frac{k_r}{k_d}, \tag{5}$$

where I_{abs} is the intensity of absorbed light, $\phi_{^1O_2}$ is the quantum yield of $^1O_2$ production, k_d is the rate constant of quenching of $^1O_2$ by DMF, k_q is the rate constant of physical quenching of $^1O_2$ by Q′, k_r is the rate constant of chemical quenching of $^1O_2$ by Q′, Q′ is quencher [Pd(bpy)(dmt)] or [Pd(phen)(dmt)], and t is irradiation time.

If the decay of Q′ is followed by visible spectroscopy, a plot of log[Q′] (or log$A$) against different irradiation time gives a straight line with the slope of k (see Eq. 4) as given in Fig. 5. If I_{abs} is not constant for different porphyrins and the k_d, k_r and the initial concentration of Q′ are kept constant in Eq. 5, the slope of log[Q′] versus irradiation time is related $I_{abs}\phi_{^1O_2}$ (yield of $^1O_2$ production). The relative yields of $^1O_2$ production for different metal hematoporphyrin IX relative to free hematoporphyrin IX were obtained from the slopes (see Fig. 5) and are given in Table 2. If the correction for the relative amounts of light absorbed by different porphyrins is made using Eq. 6, the relative efficiencies of $^1O_2$ production for

$$\frac{(\phi_{^1O_2})_2}{(\phi_{^1O_2})_1}=\frac{k_2\times(I_{abs})_1}{k_1\times(I_{abs})_2}, \tag{6}$$

different metal porphyrins referred to free porphyrin were obtained. The relative efficiencies of $^1O_2$ production follow the order: $H_2HP>PdHP>PtHP \gg NiHP$.

The irradiation of DMF solution of only [Pd(bpy)(dmt)] or [Pd(phen)(dmt)] (5×10^{-4} M) in presence of molecular oxygen or molecular nitrogen for more than 10 min shows no change in absorbance of [Pd(bpy)(dmt)] at 498 nm or [Pd(phen)(dmt)] at 500 nm. Similar irradiation of DMF solution of free hematoporphyrin IX (5×10^{-5} M) in presence of molecular oxygen or molecular nitrogen for more than 10 min shows also no change of absorbance of 498 or 500 nm.

The relative efficiencies of $^1O_2$ generation by the free base hematoporphyrin IX and its metal derivatives were further obtained by the EPR method using 2,2,6,6-tetramethyl-4-piperidinol as a chemical acceptor of $^1O_2$.[16] This method has advantage that 2,2,6,6-tetramethyl-4-piperidinol is a specific quencher of $^1O_2$, which does not react with superoxide ions, hydrogen peroxide and hydroxyl radicals.[16,20] In this method a solution of a free base porphyrin or a metal porphyrin (5×10^{-5} M) and 2,2,6,6-tetramethyl-4-piperidinol (2.5×10^{-3} M) was irradiated on the merry-go-round apparatus[3] for different irradiation time. The photoproduction of $^1O_2$ was measured by recording the EPR spectra of the nitroxide free radicals

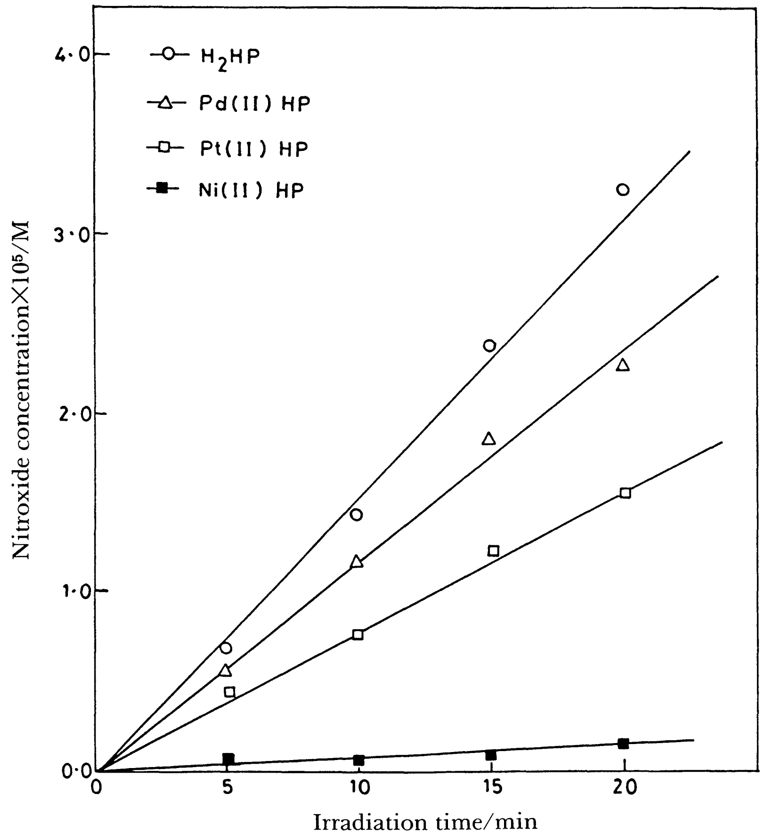

Fig. 6. Plots of XO free radical concentration versus irradiation time of DMF solution of 2,2,6,6-tetramethyl-4-piperidinol (2.5×10^{-3} M) and porphyrins (5×10^{-5} M).

generated by the reaction of 2,2,6,6-tetramethyl-1,4-piperidinol with $^1O_2$.[3,21] The linear plots of amount of nitroxide radicals produced for a free base hematoporphyrin IX and its metal derivatives versus irradiation time are given in Fig. 6. Hematoporphyrin IX gives the largest slope and the NiHP gives the smallest slope. The relative yields and relative efficiencies of $^1O_2$ production for different metal hematoporphyrin IX, as compared to free hematoporphyrin IX are given in Table 2.

The relative yields or relative efficiencies of $^1O_2$ production by the porphyrins follow the order: $H_2HP > PdHP > PtHP \gg NiHP$. This order is same as obtained above using [Pd(bpy)(dmt)] and [Pd(phen)(dmt)] as chemical quenchers.

The above results suggest that PdHP and PtHP are expected to have the energy of their $^3B_{1g}$ state arising from the d-d transition of d^8 configuration of metal ion in a square planar crystal field well above the first triplet state of porphyrin arising from π-π^* transition.[15] On the other hand NiHP shows virtually no photosensitizing ability to produce $^1O_2$ because its ligand-field $^3B_{1g}$ state has energy just lower than that of phosphorescent triplet state of porphyrin. The ligand-field $^3B_{1g}$ state provides the pathway of radiationless decay and thus reduces very considerably the transfer of energy from $^3O_2$ to produce $^1O_2$. The higher efficiency of PdHP as compared to PtHP may be due to longer lifetime of triplet state of former than later.[22]

Conclusion

The above study shows that the Pd(II) and Pt(II) complexes of α-diimine ligands with 3,4-naphthalenediol dianion can sensitize the photooxidation of 2,2,6,6-tetramethyl-4-piperidinol involving $^1O_2$ as intermediate. This intermediate is produced by energy transfer from triplet state of LLCT transition of the complexes to molecular oxygen. In addition [Pd(nn)(dmt)] as chemical quenchers of $^1O_2$ can be used in determining the relative efficiency of $^1O_2$ production sensitized by porphyrins.

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References

1) A. Vogler and H. Kunkely, *J. Am. Chem. Soc.*, **103**, 1559 (1981).

2) A. Vogler and H. Kunkely, *Angew. Chem., Int. Ed. Engl.*, **20**, 386 (1981).

3) S. Shukla, S. S. Kamath, and T. S. Srivastava, *J. Photochem. Photobiol., A, Chem.*, **117**, 287 (1989).

4) K. H. Puthraya and T. S. Srivastava, *Polyhedron*, **4**, 1579 (1985).

5) K. H. Puthraya and T. S. Srivastava, *J. Indian Chem. Soc.*, **LXII**, 843 (1985).

6) S. Shukla, S. S. Kamath, and T. S. Srivastava, *J. Photochem. Photobiol., A, Chem.*, **50**, 199 (1989).

7) S. Shukla and T. S. Srivastava, *J. Photochem. Photobiol., A, Chem.*, **48**, 249 (1989).

8) S. S. Kamath, V. Uma, and T. S. Srivastava, *Inorg. Chim. Acta*, **166**, 91 (1989).

9) A. Zweig and W. A. Henderson, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 717 (1975).

10) J. P. Macquet and T. Theophanides, *Can. J. Chem.*, **51**, 219 (1973).

11) L. Edwards, D. H. Dolphin, M. Gouternan, and A. D. Adler, *J. Mol. Spectrosc.*, **38**, 16 (1971).

12) B. S. Furniss, A. J. Hannafort, V. Rogers, P. W. G. Smith, and A. B. Tuchel, "Vogel's Textbook of Practical Organic Chemistry," Longman, London (1978), pp. 264—279.

13) I. Diamond, S. G. Graneth, and A. F. McDonagh, *Biochem. Med.*, **17**, 121 (1977).

14) B. Ranby and J. F. Rebek, "Singlet Oxygen," Wiley, New York (1978), pp. 60—110.

15) D. Eastwood and M. Gouterman, *J. Mol. Spectrosc.*, **35**, 359 (1970).

16) Y. Lion, S. Gandin, and A. Van de Voorst, *Photochem. Photobiol.*, **31**, 305 (1980).

17) K. M. Smith, "Porphyrins and Metalloporphyrins," Elsevier, Amsterdam (1975), pp. 667—700.

18) T. S. Srivastava and S. Shukla, *Proc. Indian Acad. Sci., (Chem. Sci.)*, **102**, 329 (1990).

19) E. Gandin, Y. Lion, and A. Van de Voorst, *Photochem. Photobiol.*, **37**, 271 (1983).

20) A. Rigo, E. Argese, R. Stenanto, E. F. Orsega, and P. Viglino, *Inorg. Chim. Acta*, **24**, L71 (1977).

21) S. Cannistraro, A. Van de Voorst, and G. Jori, *Photochem. Photobiol.*, **28**, 257 (1978).

22) M. Gouterman, "Excited States of Matter," ed by C. W. Shoppee, Texas Tech. Univ., Lubbock, Texas (1973), Vol. 2, pp. 63—101.