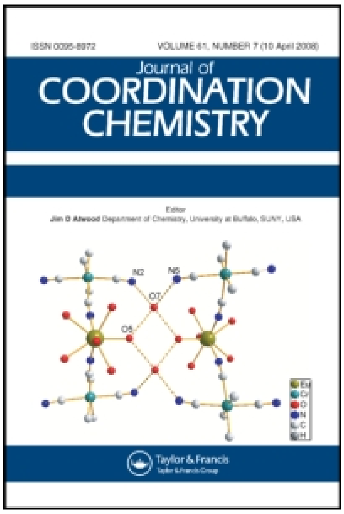

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Photochemical Behavior of Platinum(II) and Palladium(II) Complexes of 4,4'-Dimethyl-2,2'-Bipyridine

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To cite this Article Anbalagan, Victor(2003) 'Photochemical Behavior of Platinum(II) and Palladium(II) Complexes of 4,4'-Dimethyl-2,2'-Bipyridine', Journal of Coordination Chemistry, 56: 3, 161 — 172
To link to this Article: DOI: 10.1080/0095897021000039061
URL: http://dx.doi.org/10.1080/0095897021000039061

J. Coord. Chem., 2003, Vol. 56, No. 3, pp. 161–172

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PHOTOCHEMICAL BEHAVIOR OF PLATINUM(II) AND PALLADIUM(II) COMPLEXES OF 4,4′-DIMETHYL-2,2′-BIPYRIDINE

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(Received 2 November 2001; Revised 11 April 2002; In final form 20 August 2002)

Several mixed-ligand complexes of formula [MX_2(MBPY)] {where M is Pd(II) or Pt(II); X is Cl^-, I^-, N_3^-or NO_2^- and MBPY is 4,4′-dimethyl-2,2′-bipyridine} have been prepared. The UV-Vis spectra of these complexes were found to show a low-lying MLCT band and on irradiation at the MLCT band these complexes sensitize the oxidation of 2,2,6,6-tetramethyl-4-piperidinol (XH) in *N*,*N*-dimethylformamide (DMF) to 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinoloxy free radical (XO). This photo-oxidation reaction involves singlet molecular oxygen ($^1O_2$) as an intermediate and its presence was confirmed by quenching studies using bis(diethyldithiocarbamato)nickel(II) [Ni$(DDTC)_2$], a well-known $^1O_2$ quencher. The ability of the complexes to photosensitize the above photo-oxidation reaction follows the order: *[Pt*$(N_3)_2$*(MBPY)] (2)*$\sim$*[Pt*$(NO_2)_2$*(MBPY)] (3)* > *[Pt*Cl_2*(MBPY)] (4)* > *[Pt*I_2*(MBPY)] (1)* > *[Pd*$(NO_2)_2$*(MBPY)] (7)*$\sim$*[Pd*$(N_3)_2$*(MBPY)] (6)* > *[Pd*Cl_2*(MBPY)] (8)* > *[Pd*I_2*(MBPY)] (5)*, which reflects the nature of the metal ion and the nature of the ligands present in the complexes.

Keywords: Platinum(II) complexes; Palladium(II) complexes; MLCT; Singlet oxygen

INTRODUCTION

Photolysis of metal complexes and organometallic compounds is an interesting area of research in inorganic chemistry. Many metal complexes produce radicals and active oxygen species on irradiation. Active oxygen species include superoxide radical, superoxide anion and singlet molecular oxygen, etc. Among the active oxygen species, reactivity of singlet oxygen is well-studied and known to play a vital role in many photosensitized oxidative processes in biological as well as chemical systems. Some of the important applications of singlet oxygen in chemistry include photo-oxidation of sulfides [1], thiols [2], phenols [3], olefins [4] and many other organic compounds [5]. It is well established that singlet oxygen is the initial agent in photodynamic therapy of cancer [6]. Due to the importance of singlet oxygen in oxidation processes of various chemical and biological molecules it has acquired considerable significance. Many photosensitizers with varying degree of quantum yields have been reported in

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ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897021000039061

the literature. However, porphyrins and phthalocyanins are widely used as photsensitizers [7] due to their high quantum yields of singlet oxygen formation. Several complexes of d^6 ion with α-diimine ligands were also reported to be very efficient sensitizers for the generation of singlet oxygen [8]. Few metal complexes containing d^8 metal ions were reported to sensitize the photogeneration of singlet oxygen [9]. In these complexes the ligands used are α-diimines and derivatives of catechol. Here, the excited state arising from ligand-to-ligand charge-transfer (LLCT) or metal-to-ligand charge-transfer (MLCT) transition is stated to be responsible for the production of singlet oxygen. It is also reported that the dianionic catecholate ligand does not play a major role in influencing the quantum yields of singlet oxygen generation [9c]. I have found that when the excited state is MLCT, the anionic ligands also play a key role in the quantum yield of singlet oxygen production. Many complexes of Pt(II) and Pd(II) have been reported to possess anticancer activity through their substantial interaction with DNA [10]. Thus, it can be understood that Pt(II) and Pd(II) complexes can act against cancer both as cytotoxic drugs and photodynamic therapeutic agents. Since the platinum drugs are toxic, it may be possible to use a lower dosage of these drugs provided they can act as both cytotoxic drugs (via physical interaction with DNA) and phototherapuetic agents. This article reports, the photosensitizing ability of a series of complexes of platinum(II) and palladium(II) containing 4,4′-dimethyl-2,2′bipyridine (MBPY) ligand and Cl^-, I^-, N_3^- or NO_2^- as various anionic ligands.

EXPERIMENTAL

Starting Materials

Potassium tetrachloroplatinate(II) (Strem, USA), palladium chloride, sodium azide, silver nitrate, potassium chloride, 4,4′-dimethyl-2,2′-bipyridine, potassium iodide, sodium nitrite (Glaxo, India), hematoporphyrin-IX (Sigma, USA), 2,2,6,6-tetramethyl-4-piperidinol and 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinoloxy free radical (Aldrich, USA) were of reagent grade and were used as received. Bis(diethyldithiocarbamato)nickel(II), [Ni(DDTC)$_2$] was prepared according to the method reported by Furue and Russell [11]. Acetonitrile and *N*,*N*-dimethylformamide (DMF) were of spectroscopic grade and were used as received. Solvents other than the above were purified by standard procedures [12]. Spectroscopic grade solvents were used for conductivity, spectral and photochemical measurements.

Synthetic Procedures

[PtI$_2$(MBPY)] (1)

K_2PtCl_4 (1 mmol, 415 mg) was dissolved in 100 mL of double-distilled water. Potassium iodide (4 mmol, 664 mg) was added to this and the contents were stirred for half an hour followed by filtration. A warm DMF solution of MBPY (1 mmol, 184.2 mg) was added to the filtrate with constant stirring. The reaction mixture was stirred for an additional 3 h and the resultant precipitate was filtered off. The precipitate was washed with water, methanol and finally with ether. The product was recrystallized from DMF and dried in a vacuum desiccator over anhydrous calcium chloride.

[Pt(N_3)$_2$(MBPY)] (2), [Pt(NO_2)$_2$(MBPY)] (3) and [PtCl_2(MBPY)] (4)

These complexes were synthesized by the general procedure outlined below.

[PtI_2(MBPY)] (0.2 mmol, 126.6 mg) was suspended in 50 mL of double-distilled water. To the suspension, silver nitrate (0.4 mmol, 67.94 mg) was added and the mixture was stirred for 24 h in dark. The precipitated silver iodide was removed by filtration. To this filtered aqua complex, *[Pt(H_2O)$_2$(MBPY)](NO_3)$_2$*, NaN_3 (0.4 mmol, 26 mg), or $NaNO_2$ (0.4 mmol, 27.6 mg) or NaCl (0.4 mmol, 23.4 mg) was added. The solution was stirred overnight at room temperature during which time crystals of (*2*), (*3*) or (*4*) were separated. The crystals were filtered, washed with double-distilled water, methanol and ether and were dried in vacuum desiccator over anhydrous calcium chloride.

[PdCl_2(MBPY)] (8)

Palladium chloride (1 mmol, 177.3 mg) was suspended in 100 mL of double-distilled water. To this, sodium chloride (4 mmol, 234 mg) was added and the contents were stirred 30 min and filtered. A methanolic solution of MBPY (1 mmol, 184.2 mg) was added to the filtrate with constant stirring. The reaction mixture was stirred for an additional 3 h and the resultant precipitate was filtered off, washed with water, methanol and finally with ether. The product was recrystallized from DMF and dried in vacuum desiccator over anhydrous calcium chloride.

[PdI_2(MBPY)] (5), [Pd(N_3)$_2$(MBPY)] (6) and [Pd(NO_2)$_2$(MBPY)] (7)

These complexes were synthesized by the general method given below.

[PdCl_2(MBPY)] (0.2 mmol, 72.3 mg) was suspended in 20 mL of double-distilled water. To the suspension, silver nitrate (0.4 mmol, 67.94 mg) was added and the mixture was stirred for 3 h in dark. The precipitated silver chloride was removed by filtration. The filtered aqua complex, *[Pd(H_2O)$_2$(MBPY)] (NO_3)$_2$*, was dried under vacuum. The aqua complex (0.2 mmol, 90.12 mg) was taken in 25 mL of double-distilled water and to this, KI (0.4 mmol, 66.4 mg) or NaN_3 (0.4 mmol, 26 mg), or $NaNO_2$ (0.4 mmol, 27.6 mg) was added. The reaction mixture was stirred for 8 h. The Complexes (*5*), (*6*) and (*7*) precipitated out during this time. The resultant precipitate was filtered, washed with double-distilled water, methanol and ether. The compounds were dried in a vacuum desiccator over anhydrous calcium chloride.

Physical Measurements

Microanalyses for carbon, hydrogen and nitrogen were performed by M-H-W Laboratories, Phoenix, AZ. Conductivity measurements of 10^{-3} M solutions of the complexes were carried out in acetonitrile using Systronics conductivity bridge 305. The infrared spectra as KBr pellets were recorded on Perkin-Elmer-681 infrared spectrophotometer in the range 4000–600 cm^{-1}. Electronic absorption spectra of the complexes were recorded on Shimadzu UV-265 UV-Vis spectrophotometer. The proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian VXR-300 NMR spectrometer in deuterated dimethyl sulfoxide (DMSO-d_6) with tetramethyl silane (TMS) as an internal standard. All the spectra were recorded in the range of 0–10 ppm. The electron paramagnetic resonance (EPR) spectra of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinoloxy free radical (XO), a nitroxide free radical, formed by the reaction of 2,2,6,6-tetramethyl-4-piperidinol (XH) with singlet molecular oxygen ($^1O_2$) [13] were recorded on a Varian E-12 ESR spectrometer (X-band) using an aqueous EPR cell (Varian E-248). The EPR measurements were quantified by comparing the spectrum of a solution of unknown concentration of nitroxide free radical (XO) with the spectrum of known concentrations of nitroxide free radical (XO) under identical instrumental conditions. The photochemical experiments were repeated three times for consistency and the error on quantum yields are in the range of 0–5%.

General Irradiation Procedure

The photochemical experiments of metal complexes were carried out on a merry-go-round apparatus. It consists of a tungsten halogen lamp (250 W × 24 V), operating at 20 V, fixed at the center of a double-jacketed Pyrex vessel thermostatically controlled at 28 ± 1°C by circulating water. The solutions to be irradiated (range 300–800 nm) were placed in Pyrex glass tubes (20 cm × 1 cm) fitted on the merry-go-round apparatus 5 cm away from the light source at a fixed speed of 33 revs. per second.

DMF solutions of the complexes (1×10^{-4} M) and XH (1×10^{-2} M) were bubbled with solvent-saturated molecular oxygen for 15 min. The oxygen-saturated solutions were placed in Pyrex glass tubes and irradiated on the merry-go-round apparatus for different time intervals. The $^1O_2$ formed reacts with XH to form nitroxide radical (XO); the EPR spectra of the solutions were recorded. The amount of XO radicals formed was calculated by comparing the EPR spectra with the spectrum of a solution of known nitroxide radical concentration. Various control experiments were performed by irradiating the solutions containing (a) the metal complex and XH saturated with argon, (b) only metal complex saturated with oxygen and (c) only XH saturated with oxygen.

The quenching experiments were performed using bis(diethyldithiocarbamato)-nickel(II), [Ni(DDTC)$_2$] as the physical quencher of $^1O_2$. The metal Complex *2* (1×10^{-4} M), different concentrations of XH ranging from 1×10^{-3} to 1×10^{-2} M and different concentrations of the quencher ($Q_1 = 2 \times 10^{-5}$ M and $Q_2 = 1 \times 10^{-5}$ M) were placed in Pyrex glass tubes and saturated with molecular oxygen for 15 min. Subsequently, the solutions were irradiated for 1 h with mixing at 5 min intervals. The EPR spectra of these samples gave the amount of XO free radical formed.

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes (*1–8*)

Mixed-ligand complexes of the type [MX$_2$(MBPY)] {where M is Pd(II) or Pt(II); X is Cl$^-$, I$^-$, N_3^- or NO_2^- and MBPY is 4,4′-dimethyl-2,2′-bipyridine} have been prepared. In general these complexes were prepared from the aqua complexes. The aqua complex of Pd(II), [Pd(H$_2$O)$_2$(MBPY)](NO$_3$)$_2$ was prepared from [PdCl$_2$(MBPY)] and that of Pt(II) was prepared from [PtI$_2$(MBPY)]. These aqua complexes were treated with the salts of the anionic ligands to get the relevant complexes.

The conductivity measurements of 10^{-3} M solution of these complexes have been carried out in acetonitrile. The molar conductance values are in the range of

TABLE I Analytical, molar conductance and ^1H NMR spectral data of *1–8*

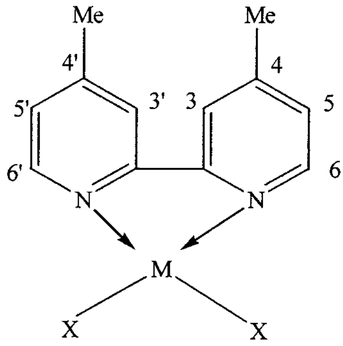
Complex	*MBPY protons* (in ppm)[a]				*Molar conductance*[b]	*Yield* (%)	*Elemental analysis*[c]		
	$H_{3,3'}$	$H_{4,4'}$	$H_{5,5'}$	$H_{6,6'}$			C	H	N
1	8.47(s)	2.46(s)	7.27(d)	9.84(d)	5	84	22.95 (22.77)	1.89 (1.91)	4.41 (4.42)
2	8.41(s)	2.48(s)	7.63(d)	8.30(d)	4	21	30.78 (31.12)	2.57 (2.61)	24.16 (24.19)
3	8.50(s)	2.57(s)	7.66(d)	8.24(d)	7	39	30.62 (30.59)	2.53 (2.56)	12.07 (11.89)
4	8.44(s)	2.48(s)	7.66(d)	9.25(d)	5	40	32.39 (32.03)	2.64 (2.68)	6.18 (6.22)
5	8.48(s)	2.52(s)	7.26(d)	9.54(d)	7	46	26.43 (26.50)	2.19 (2.22)	5.06 (5.15)
6	8.39(s)	2.51(s)	7.61(d)	8.30(d)	5	40	38.27 (38.53)	3.30 (3.23)	29.98 (29.96)
7	8.48(s)	2.53(s)	7.60(d)	7.94(d)	7	52	37.55 (37.73)	3.14 (3.16)	14.66 (14.66)
8	8.42(s)	2.52(s)	7.60(d)	8.88(d)	8	91	39.95 (40.03)	3.34 (3.36)	7.75 (7.78)

[a]Solvent, DMSO-d^6; s, singlet; d, doublet. [b]Molar conductance in acetonitrile, $cm^2\,ohm^{-1}\,mol^{-1}$. [c]Calculated values are given in parentheses.

3–10 $cm^2\,ohm^{-1}\,mol^{-1}$. This suggests that these mixed-ligand complexes are nonelectrolytes [14]. The molar conductance, percentage yields of synthesis, elemental analysis and proton NMR spectral data of these complexes are given in Table I.

The IR spectra of these metal complexes were recorded as KBr pellets. The Complexes (*2*) and (*6*) show a strong band at 2020 and 2040 cm^{-1}, respectively, which are due to the stretching vibrations of the coordinated azide. The strong band observed at 1350 cm^{-1} for both (*3*) and (*7*) is due to coordinated nitrite [15]. The above complexes show several C–H stretching modes between 3450 and 2840 cm^{-1} indicating the presence of MBPY. The shifts and the changes in intensity of certain vibrational frequencies of ligands in the complexes as compared to free MBPY indicate that the MBPY is coordinated to metal ions in the complexes [16–18].

The ^1H NMR spectra of the complexes were recorded in deuterated dimethylsulfoxide (DMSO-d_6). The structure and numbering scheme of the ligand protons of the complexes are given in Fig. 1. The ^1H NMR spectra of these complexes indicate deshielding of aromatic protons of the ligand MBPY on coordination with palladium(II) and platinum(II). In the ^1H NMR spectra of [MX_2(MBPY)], (X is Cl^-, I^-, N_3^- or NO_2^-) all the protons of MBPY experience downfield shifts, when compared to the free ligand [19]. The protons $H_{5,5'}$ and $H_{6,6'}$ show a doublet while $H_{3,3'}$ show a singlet in all these complexes and the free MBPY. The methyl protons show a singlet, which merges with the DMSO-d_6 peak in some of the cases. The chemical shifts of MBPY protons of azido and nitrito complexes when compared with the corresponding chloro complexes show an upfield shift. This behavior is due to stronger bonding of these ligands (azide and nitrite) to metal ion than chloride and more back bonding from metal *d*-orbital to the MBPY ligand in the former complexes. The integrated areas obtained for the protons in complexes correspond to the proposed stoichiometry of the complexes. The $^3J(^{195}Pt–^1H)$ couplings in the platinum(II) complexes at 300 MHz could not be observed due to decrease of chemical shielding anisotropy with increase in magnetic field strength [20].



Complex	M	X
1	Pt^{II}	I^-
2	Pt^{II}	$(N_3)^-$
3	Pt^{II}	$(NO_2)^-$
4	Pt^{II}	Cl^-
5	Pd^{II}	I^-
6	Pd^{II}	$(N_3)^-$
7	Pd^{II}	$(NO_2)^-$
8	Pd^{II}	Cl^-

FIGURE 1 Structure and numbering scheme of protons of complexes of Pt(II) and Pd(II).

The proton NMR spectral data, IR, molar conductance and elemental analysis data confirm the synthesis and structures assigned to these complexes.

The electronic absorption spectra of these complexes in DMF were recorded and one of the representative spectra is produced in Fig. 2. The electronic absorption spectra of the complexes generally show four bands between 200 and 900 nm. Usually, three bands in the UV region and one low-lying band in the region of 350–450 nm are observed. In the case of complexes such as $[MCl_2(Py)]$ [21] (Py = pyridine; M = Pt(II) or Pd(II) and of $[MX_2(N\text{–}N)]$[22] (N–N = α-diimine; M = Pt(II) or Pd(II); X = Cl^-, Br^- or I^-), the HOMO (highest occupied molecular orbital) is predominantly the $d_{x^2-y^2}$ orbital and LUMO (lowest unoccupied molecular orbital) is the π^* orbital of α-diimine. A corresponding assignment made for the $[MX_2(MBPY)]$ complexes indicates that the transition between HOMO and LUMO leads to a charge transfer transition

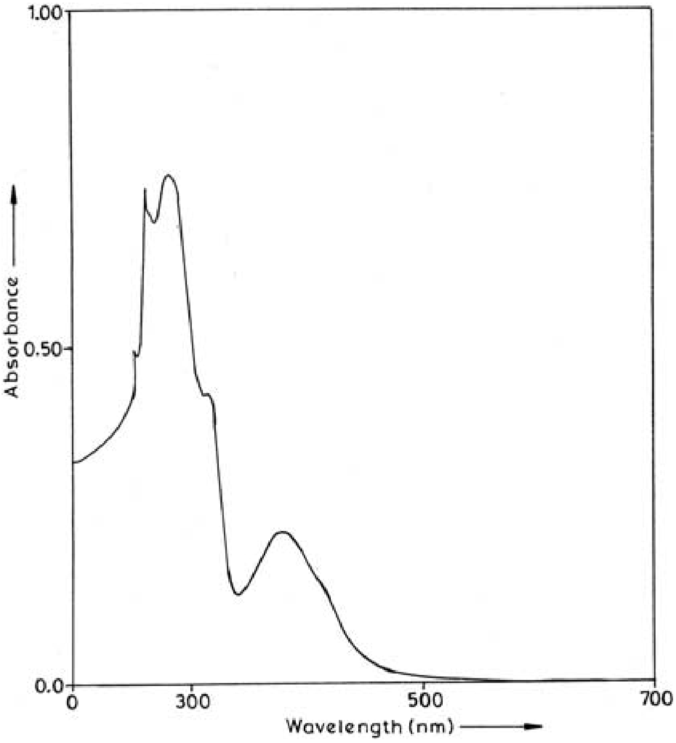


FIGURE 2 Electronic absorption spectrum of *1* (4×10^{-5} M) in DMF.

corresponding to the lowest energy band in the spectra of [MX_2(MBPY)]. This assignment was further confirmed by solvent studies [23]. The position of the low-energy MLCT bands of these complexes are collected in Table II.

Photolysis

Determination of the Efficiency of Generation of $^1O_2$

Molecular oxygen-saturated DMF solutions of the complexes (1×10^{-4} M) and XH (1×10^{-2} M) were irradiated with light (300–800 nm) for different intervals of time in a merry-go-round apparatus. The $^1O_2$ molecules formed combine with XH molecules to form XO free radicals, which were measured by the EPR method [13]. The solution before irradiation and the solution kept in dark gave no EPR signal, but the irradiated solution exhibits three equidistant EPR peaks of equal intensity, indicating the formation of XO radicals. There is a linear relationship between the amount of free radical formed and the irradiation time intervals. Plots of the amount of XO radical formed against time of irradiation for each complex are given in Fig. 3. The slope of the plot gives the amount of $^1O_2$ formed. Relative efficiencies of $^1O_2$ formation were calculated after correcting for the amount of light absorbed by the metal complexes. The relative efficiencies normalized to *2* are given in Table II. The efficiencies of the complexes for the photogeneration of $^1O_2$ lie in the following order:

$$2 \sim 3 > 4 > 1 > 7 \sim 6 > 8 > 5.$$

TABLE II MLCT band maxima, quantum yields and efficiencies of photogeneration of $^1O_2$ in DMF of *1–8*

Complex	*MLCT band maxima (λ_{max}) in* nm	*Relative quantum yield of $^1O_2$ production normalized to 2*	*Relative efficiency*[b] of $1O_2$ production normalized to *2*
1	382 (5.6)[a]	62.9	47.6
2[c]	391 (4.7)	100.0	100.0
3	362 (0.8)	88.6	99.5
4	384 (2.8)	64.3	67.7
5	369 (3.2)	14.3	11.5
6	349 (3.8)	45.7	43.5
7	373 (2.3)	40.7	44.3
8	362 (0.6)	25.7	30.6

[a] Molar absorptivity in $\varepsilon \times 10^{-3}$ L mol^{-1} cm^{-1} is given in parentheses. [b] Relative integrated areas under absorption curves between 300 and 800 nm of *1*, *2*, *3*, *4*, *5*, *6*, *7* and *8* for 1×10^{-4} M solutions are in the ratio of 1.32 : 1.00 : 0.89 : 0.95 : 1.24 : 1.05 : 0.92 : 0.84. [c] Efficiency of photogeneration of $^1O_2$ is about 34.6% of that of Hematoporphyrin-IX after correction of relative amounts of light absorbed.

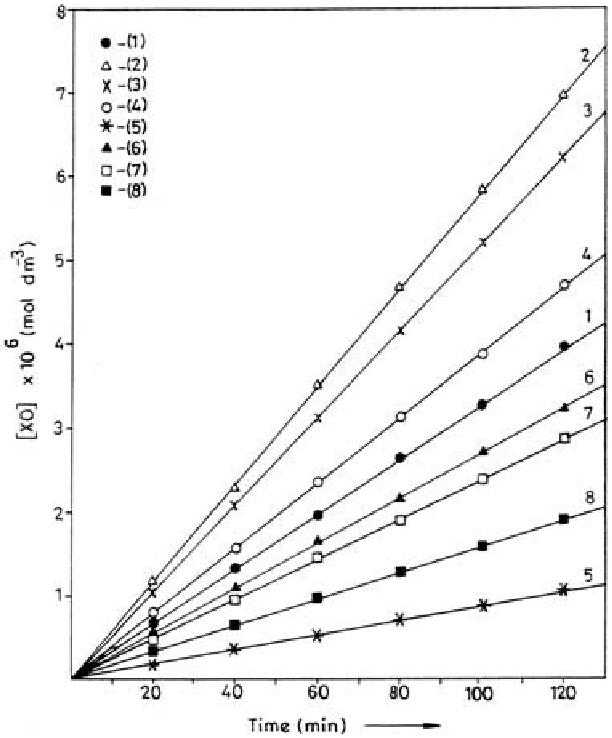


FIGURE 3 Plots of XO free radical concentration *vs* irradiation time intervals of solutions of *1–8* (1×10^{-4} M) in the presence of XH (1×10^{-2} M) in DMF.

The following mechanism is suggested for the photo-oxidation reaction,

$$
\begin{aligned}
&{}^1S_0 \xrightarrow{h\nu} {}^1S_1\\
&{}^1S_1 \xrightarrow{\text{ISC}} {}^3S_1\\
&{}^3O_2 + {}^3S_1 \xrightarrow{\text{ET}} {}^1S_1 + {}^1O_2\\
&{}^1O_2 \xrightarrow{k_d} {}^3O_2\\
&{}^1O_2 + \text{XH} \xrightarrow{k_r} {}^3O_2 + \text{XO}\\
&{}^1O_2 + \text{Q} \xrightarrow{k_q} {}^3O_2 + \text{Q} \quad \text{(physical quenching)}
\end{aligned}
$$

where ${}^1S_0$ is the ground state of the sensitizer (*1–8*), ${}^1S_1$, ${}^3S_1$ are its first excited singlet and triplet states respectively, $h\nu$ is the energy of a photon, ISC is intersystem crossing, ET is energy transfer, k_d is the rate constant of quenching of ${}^1O_2$ by DMF, k_r is the rate constant of chemical reaction of ${}^1O_2$ with XH to produce XO and k_q is the rate constant of physical quenching of ${}^1O_2$ by [Ni(DDTC)$_2$], (Q). On the basis of the above mechanism, the rate of formation of XO free radicals by oxidation of XH with ${}^1O_2$ (in the absence of quencher) using steady state approximation, can be given by

$$\mathrm{d[XO]}/dt = I_{\mathrm{abs}}\phi({}^1O_2)\{k_r[\mathrm{XH}]/(k_r[\mathrm{XH}] + k_d)\}$$

where I_{abs} is the intensity of irradiation and $\phi({}^1O_2)$ is the quantum yield of ${}^1O_2$ production. If k_r, [XH] and k_d are kept constant, the slope of the plot of the amount of nitroxide radical formed *vs* time of irradiation is directly proportional to $I_{\mathrm{abs}} \times \phi({}^1O_2)$. By using the correction for the relative amounts of light absorbed or the relative integrated areas under the absorption curves for the different complexes, the relative quantum yield can be calculated by the following equation;

$$\phi({}^1O_2)_1/\phi({}^1O_2)_2 = \{(\mathrm{slope})_2 \times (I_{\mathrm{abs}})_1\}/\{(\mathrm{slope})_1 \times (I_{\mathrm{abs}})_2\}$$

The relative integrated areas under the absorption curves for the various complexes were used to find the relative quantum yields of singlet oxygen. The quantum yields were normalized to the Complex *2* and are included in Table II. The gross features on the quantum yields of ${}^1O_2$ production can be rationalized on the basis of the following arguments.

In these complexes the HOMO is metal based ($d_{x^2-y^2}$ orbital) and the LUMO is ligand based (π^* orbital of MBPY) [21]. The ${}^1O_2$ formation may occur by energy transfer from the ${}^3(d\text{–}\pi^*)$ state of the metal complexes to molecular oxygen [24]. On moving from Pd(II) to Pt(II), the crystal field splitting increases by 30–50%. The [MX$_2$(α-diimine)] complexes have C_{2v} symmetry and their ${}^3A_2$ (${}^1A_2$) state has higher energy than the ${}^3(d\text{–}\pi^*)$ state in the platinum complexes. Thus the ${}^3A_2$ (${}^1A_2$) state is not available for radiationless decay and hence the Pt(II) complexes act as good photosensitizers. However, there is mixing of the π^* orbital of MBPY with d levels of the metal in Pd(II) complexes, thereby, providing a pathway for radiationless decay of the $^3(d\text{–}\pi^*)$ state [25,26]. This may explain the poorer sensitizing ability of Pd(II) complexes compared to their platinum counterparts. The photosensitizing ability of the complexes to generate $^1O_2$ has been compared with that of hematoporphyrin-IX. The metal Complex *2* shows an efficiency of 34.6% as compared to hematoporphyrin-IX, after correcting for the relative amounts of light absorbed. It is observed that the photosensitizing ability of the complexes depends mainly on the crystal field splitting of the central metal ion, the average ligand field strength of the mixed ligands present in the metal complex. Detection of singlet oxygen formation was not observed in the different control experiments performed with the solutions containing (a) the metal complex and XH saturated with argon gas, (b) the solutions containing only metal complexes saturated with oxygen gas and (c) the solutions containing only XH saturated with oxygen gas.

Determination of k_q

The involvement of $^1O_2$ is inferred by the absence of XO radical from the irradiated solutions of the metal complexes and XH saturated with argon, the solutions of XH saturated with oxygen gas and the solution containing the metal complex saturated with oxygen gas. However, quenching experiments were performed to confirm the formation of singlet oxygen. The quenching rate constant (k_q) of $^1O_2$ was also determined using $[Ni(DDTC)_2]$, a well-known physical quencher of singlet oxygen [11]. In these experiments, molecular oxygen saturated solutions containing *2* (1×10^{-4} M), $[Ni(DDTC)_2]$ (2×10^{-5} or 1×10^{-5} M) and different concentrations of XH (varying from 1×10^{-3} to 1×10^{-2} M) were irradiated at 300–800 nm for 1 h. The amount of XO free radical formed was measured by the EPR method [13]. 1/[XO] was plotted against 1/[XH] for two different concentrations of $[Ni(DDTC)_2]$. Two linear plots with intercepts meeting at the same point on the *y*-axis were obtained as shown in Fig. 4. The relative amount of light absorbed by the $[Ni(DDTC)_2]$ in the wavelength range of 300–800 nm, at the concentrations of 10^{-5} or 2×10^{-5} M, is less than 1% as compared with *2* and therefore there is no competition for light absorption between the sensitizer and quencher.

In the presence of quencher (Q), the quenching rate constant k_q can be calculated using the following equations:

$$^1O_2 \xrightarrow{k_d} {}^3O_2$$

$$^1O_2 + XH \xrightarrow{k_r} {}^3O_2 + XO$$

$$^1O_2 + Q \xrightarrow{k_q} {}^3O_2 + Q \quad \text{(physical quenching)}$$

Thus we have $1/[XO] = 1/[^1O_2]\ [1 + \{k_d + k_q[Q]\ /\ k_r[XH]\}]$.

From the plot of 1/[XO] against 1/[XH], we have

$$k_q = \{\text{slope} \times k_r/\{\text{intercept} \times [Q]\}\} - \{k_d/[Q]\}$$

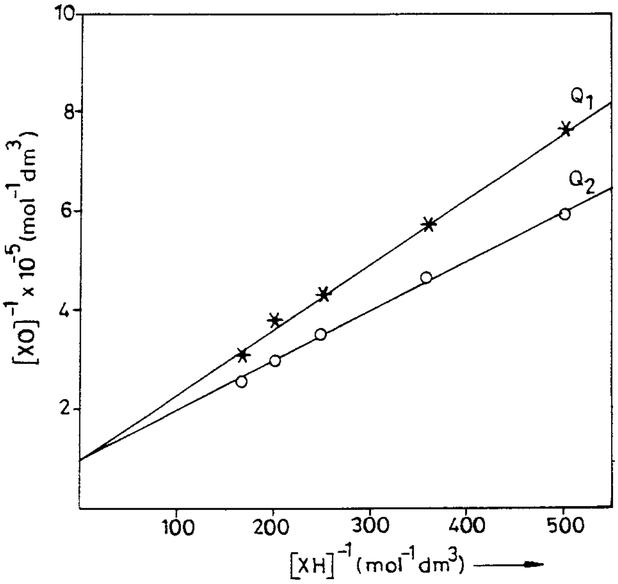


FIGURE 4 Plots of the reciprocal of XO free radical concentration *vs.* the reciprocal of XH concentration after irradiation for 1 h in the presence of [Ni(DDTC)$_2$] ($Q_1 = 5 \times 10^{-5}$ M and $Q_2 = 1 \times 10^{-5}$ M) using *2* (1×10^{-4} M) as photosensitizer.

By substituting the values of k_d and k_r ($k_d = 1.43 \times 10^5\,s^{-1}$ and $k_r = 6.72 \times 10^7\,M^{-1}\,s^{-1}$) [9c,27] and the slope and intercept {slope = $1/[^1O_2] \times \{k_q\,[Q] + k_d/k_r$ and intercept = $1/[^1O_2]\}$, k_q can be calculated. The value of k_q is found to be $3.65 \times 10^{10}\,M^{-1}s^{-1}$ and $5.42 \times 10^{10}\,M^{-1}\,s^{-1}$ for quencher concentrations of 2×10^{-5} and 1×10^{-5} M respectively. The average k_q is $4.54 \times 10^{10}\,M^{-1}\,s^{-1}$. The same intercept for different quencher concentrations indicates that primarily $^1O_2$ decay is involved and alternative processes, such as light absorption by the quencher or quenching of excited sensitizer, are not imperative [28]. The quenching of $^1O_2$ by [Ni(DDTC)$_2$] is near diffusion-controlled values, consistent with quenching due to an energy transfer process [28]. The slope increases with an increase in concentration of [Ni(DDTC)$_2$]. This suggests the physical quenching of $^1O_2$ by [Ni(DDTC)$_2$] is involved and rules out the possibility of quenching of the excited sensitizer [28].

CONCLUSION

This study reveals that the simple complexes of platinum(II) and palladium(II) can photosensitize the formation of singlet molecular oxygen. The quantum yields of singlet oxygen formation are comparable with hematoporphyrin, a recognized sensitizer for singlet oxygen. It had been reported that the quantum yields of singlet oxygen formation generally depends upon diimine ligands but not on the anionic ligands. But this study shows that the anionic ligands also play a major role in determining the quantum yields of singlet oxygen formation. Accordingly it can be said that when the photolysis involves a MLCT band, then the photochemistry can be dependent upon the anionic ligands too.

Acknowledgments

I thank Prof. T.S. Srivastava, Department of chemistry, Indian Institute of Technology, Bombay, and Prof. P.R. Ponda, Department of Chemistry, SCHM College, Ulhasnagar, for their encouragement. Financial assistance by the HSNC board, Bombay is gratefully acknowledged.

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