Inorg. Chem. **1983**, *22*, 3825-3828 **3825**

Notes

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Solvent and Substituent Effects on the Lowest Energy Excited States of $M(CO)_4$(diimine) (M = Cr, Mo, W) Complexes

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Received March 2, 1983

Solvatochromic properties of transition-metal complexes have been reported for both square-planar and octahedral complexes, for example, Ni(S(CN)C=C(Ph)S)phen,[1] Pt(bpy)X_2,[2] Pd(bpy)Cl_2,[2] *cis*-$FeL_2(CN)_2$,[3] *cis*-$Ru(bpy)_2(CN)_2$,[4] and $M(CO)_4L$[5,6] complexes, where M = Cr, Mo, or W, X = Cl, Br, or I, and L = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), diazabutadiene, or their derivatives. Although the effects of solvent and substituent on the electronic absorption spectra of transition-metal complexes are well recognized, few studies have attempted to correlate the electronic properties of these complexes with established solvent parameters.[6e] In recent years, largely through interest in their photophysical and photochemical characteristics, the low-lying excited states of group 6B metal carbonyls have received considerable attention. Several of these complexes exhibit low-energy ligand field (LF) and metal to ligand charge-transfer (MLCT) excited states, the MLCT energies being very sensitive to the nature of solvent and substituent.[6] As the photophysical and photochemical properties of several of these complexes have been shown to be dependent on the relative positions of the LF and MLCT excited states,[7] the roles of solvent and substituent are important ones.

This paper reports the results of correlating the low-lying excited state energies of $M(CO)_4L$ complexes (M = Cr, Mo, and W; L = bpy, phen, or derivative) with established solvent[8-11] and substituent[12] parameters. The $M(CO)_4L$ complexes are ideal for this type of study as they are soluble in a wide range of solvents and a variety of substituted ligands (L) are readily available. Many of these complexes, however, undergo thermal reaction in solution[13] over a period of a few minutes. We have largely overcome this drawback by employing a diode-array UV-visible spectrophotometer that rapidly records the absorption data.

Experimental Section

Materials. The metal hexacarbonyls (Strem Chemicals), 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) (Aldrich), 4-methyl-1,10-phenanthroline (4-Me-phen), 5-methyl-1,10-phenanthroline (5-Me-phen), 5-phenyl-1,10-phenanthroline (5-Ph-phen), 5-chloro-1,10-phenanthroline (5-Cl-phen), and 5-nitro-1,10-phenanthroline (5-NO_2-phen) (Alfa) were used without further purification. The solvents used were of spectroscopic grade and are all commercially available.

Synthesis of $M(CO)_4L$. The complexes were prepared by 313-nm photolysis of the parent hexacarbonyl with excess ligand in N_2-purged isooctane according to a literature procedure.[14] The products are sparingly soluble in isooctane and precipitate out of solution. Purification was achieved by washing the product several times with isooctane. Further purification by column chromatography on alumina (Fisher, 80-200 mesh) was needed in some cases to obtain pure samples. Elemental (C, H, N) analyses were satisfactory for several representative compounds. UV-visible absorption spectra agree well with those published.[6a] The compounds were reasonably stable as solids and were stored in the dark.

Electronic Absorption Spectra. The $M(CO)_4L$ complexes exhibited varying degrees of stability in solution. In general, for any given ligand, the chromium complexes were the least stable. Thermal decomposition was particularly noticeable in the more polar coordinating solvents such as piperidine, dimethyl sulfoxide, and dimethylformamide. To minimize thermal reaction, absorption spectra were recorded within 5 s of the dissolution of the complex by using a microprocessor-controlled diode-array Hewlett-Packard 8450A UV-visible spectrophotometer.

Results and Discussion

The electronic absorption spectra of $M(CO)_4$(diimine) complexes exhibit low-lying ligand field (LF) and metal to ligand charge-transfer (MLCT) transitions.[6a] The MLCT band maxima are markedly solvent dependent; for example, solutions of $W(CO)_4$phen in dimethylformamide, tetrahydrofuran, and diethyl ether are colored yellow, orange, and red, respectively. In contrast, the higher energy LF transitions of the $M(CO)_4L$ complexes are essentially unshifted on changing the solvent medium. Solvatochromic properties of MLCT states have also been reported for other substituted metal carbonyl complexes.[15] In a very nonpolar solvent, the MLCT absorption further red-shifts and exhibits the features

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Table I. Solvent Dependence of the Metal to Ligand Charge-Transfer Absorption Maxima of $M(CO)_4bpy$ Complexes at 298 K (M = Cr, Mo, and W)

solvent	E_{MLCT}, kJ mol^{-1} Cr	Mo	W	E_T	π^*
isooctane	202.7	215.9	208.4	129.3[b]	−0.08[b]
	219.5[a]	230.9[a]	223.2[a]		
triethylamine	212.1	226.6	219.1	139.3	0.14
	228.3[a]	248.2[a]	235.0[a]		
diethyl ether	224.0	241.2	231.8	144.8	0.27
piperidine	228.3	245.1	236.4	148.5	
tetrahydrofuran	236.4	253.4	245.1	156.5	0.58
3-pentanone	242.2	259.0	251.3	164.4	
cyclohexanone	241.2	258.4	250.3	170.7	0.76
acetone	246.1	263.5	256.7	176.6	0.71
dimethylacetamide	253.4	269.4	262.3	182.8	0.88
dimethylformamide	255.6	270.6	263.5	183.3	0.88
dimethyl sulfoxide	261.2	273.1	265.8	188.3	1.00
mesitylene	219.9	236.4	228.3	138.5	0.41
toluene	224.0	240.7	230.9	141.8	0.54
benzene	225.7	243.1	232.7	144.4	0.59
2-picoline	240.7	256.7	248.2	160.3	
pyridine	244.1	261.2	254.5	168.2	0.87
tetrachloroethylene	208.4	221.5	215.2	133.5	0.28
	223.2[a]	233.6[a]	229.2[a]		
carbon tetrachloride	204.1	222.3	214.8	136.0	0.29
	219.1[a]	236.4[a]	229.2[a]		
trichloroethylene	218.3	235.9	227.4	150.2	0.53
chlorobenzene	230.0	247.7	238.8	156.9	0.71
o-dichlorobenzene	230.9	249.7	239.7	159.4	0.80
chloroform	228.7	245.6	236.9	163.6	0.58
methylene chloride	238.3	254.5	249.2	172.0	0.83
1,2-dichloroethane	238.3	256.1	247.7	175.3	0.81
2-methyl-2-propanol[c]	228.7	247.2	241.2	183.7	0.41
cyclohexanol	231.8	250.8	240.2	196.2	
3-phenyl-1-propanol	228.3	254.0	242.2	202.9	
2-propanol	229.2	250.8	238.8	203.3	0.46
1-pentanol	226.6	244.6	238.3	205.4	
1-butanol	232.7	248.7	243.1	210.0	0.46
benzyl alcohol	239.2	257.8	249.2	212.6	0.98
ethanol	235.0	254.5	250.3	217.2	0.54
methanol	242.2	260.0	252.4	232.2	0.60

[a] Higher energy component observed as a shoulder. [b] See ref 19. [c] Data recorded at 303 K.

of two components. Previously recorded absorption spectra of these complexes in EPA at 77 K exhibit similarly resolved features,[6d] and recently resonance Raman and magnetic circular dichroism measurements have indicated that the MLCT band comprises several electronic transitions.[16] There is thus considerable evidence that the $M(CO)_4$(diimine) complexes each have at least two low-energy MLCT excited states.

The MLCT absorption maxima for $M(CO)_4bpy$ (M = Cr, Mo, and W) in the full range of solvents studied are shown in Table I. These complexes show trends that are general for $M(CO)_4L$. For any particular ligand and solvent, the energies of the MLCT absorption (E_{MLCT}) are ordered Mo > W > Cr, congruent with other types of group 6B metal carbonyl complexes.[17] The nature of the metal center in $M(CO)_4bpy$ does not appear to significantly influence the solvent sensitivity of the MLCT state; each complex exhibits shifts of up to 50 ± 0.3 kJ mol^{-1} over the full solvent range.[18]

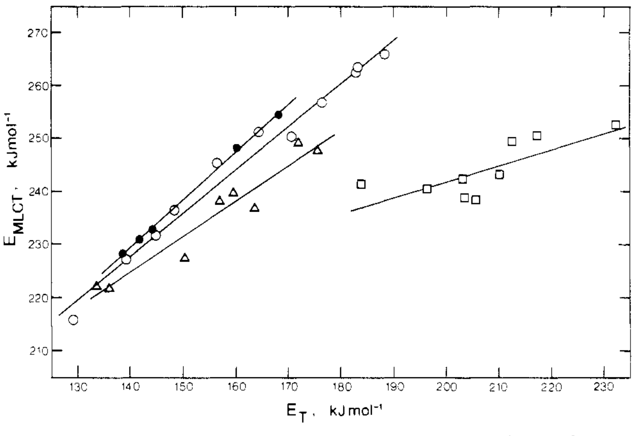

Figure 1. Energies of the MLCT absorption (E_{MLCT}) of $W(CO)_4bpy$ plotted against E_T solvent values: △, chlorinated solvents; □, alcohols; ○, aliphatic solvents; ●, aromatic solvents.

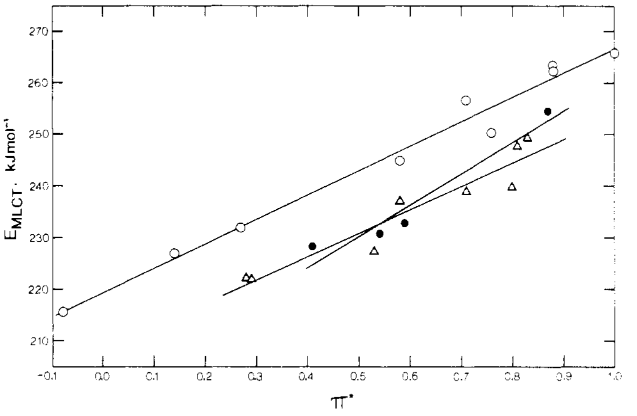

Figure 2. Energies of the MLCT absorption (E_{MLCT}) of $W(CO)_4bpy$ plotted against π^* solvent values: △, chlorinated solvents; ○, aliphatic solvents; ●, aromatic solvents.

Literature values of Reichardt's solvent parameters (E_T)[10] and Kamlet and Taft's solvent polarity scale (π^*)[11] are incorporated in Table I. The results of correlating the MLCT energies (E_{MLCT}) of $W(CO)_4bpy$ with E_T and π^* are shown in Figures 1 and 2. The $W(CO)_4bpy$ results are representative of all the $M(CO)_4$(diimine) series, and the following discussion pertains to all the complexes in this study. The best least-squares fits for E_{MLCT} vs. E_T were obtained by separately plotting chlorinated solvents (slope 0.671, correlation coefficient 0.965), alcohols (slope 0.302, correlation coefficient 0.775), other aliphatic solvents (slope 0.816, correlation coefficient 0.991),[18,19] and other aromatic solvents (slope 0.904, correlation coefficient 0.999) (Figure 1). The best least-squares fits for E_{MLCT} vs. π^* were obtained by separately plotting chlorinated solvents (slope 45.06 kJ mol^{-1}, correlation coefficient 0.951), other aliphatic solvents (slope 47.17 kJ mol^{-1}, correlation coefficient 0.990),[18,19] and other aromatic solvents (slope 60.27 kJ mol^{-1}, correlation coefficient 0.968) (Figure 2). There is an insufficient range of accurate π^* values available for the alcohols to obtain a meaningful correlation.[11a] In either the E_T or π^* plots, the correlations of the least-squares regression lines were not significantly improved by further segregating the solvents. The results show that the position of the MLCT absorption depends on the type of solvent in addition to the solvent polarity. Plots of E_{MLCT} vs. dielectric constant (ϵ)[8] and Kosower's solvent parameter (Z)[9] were not observed to correlate to the degree of E_T and π^* and were not

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(18) A mean value of E_{MLCT} was used for the solutions exhibiting two MLCT components.

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Table II. Solvent Dependence of the Metal to Ligand Charge-Transfer Absorption Maxima of $W(CO)_4L$ Complexes at 298 K (L = 1,10-Phenanthroline and Derivatives)

solvent	E_{MLCT}, kJ mol^{-1} 4-Me-phen	phen	5-Me-phen	5-Ph-phen	5-Cl-phen	5-NO_2-phen
isooctane	215.9	212.1	212.9	212.1	205.5	202.1
	230.0[a]	231.8[a]	231.8[a]	231.8[a]	226.6[a]	219.9[a]
triethylamine	224.9	221.5	220.7	218.3	215.2	213.6
	244.1[a]	241.2[a]	239.2[a]	232.7[a]	231.8[a]	229.2[a]
diethyl ether	236.4	232.7	233.2	232.3	227.4	223.2
piperidine	240.7	236.4	236.4	233.6	230.9	241.2
tetrahydrofuran	249.2	245.1	244.1	242.6	238.3	235.9
3-pentanone	255.6	251.3	250.3	247.2	245.1	242.2
cyclohexanone	255.6	250.3	251.3	249.2	244.1	241.2
acetone	262.3	257.8	256.7	257.8	250.3	246.1
dimethylacetamide	267.0	262.3	261.8	259.0	254.0	250.3
dimethylformamide	267.0	263.5	262.3	261.8	256.1	251.8
dimethyl sulfoxide	268.8	265.8	265.2	264.1	259.5	255.1
mesitylene	233.6	229.2	228.7	227.9	223.6	220.3
toluene	236.9	233.6	233.2	231.4	227.9	224.0
benzene	238.3	234.6	234.6	233.6	229.2	225.7
2-picoline	254.0	249.2	248.7	246.1	241.7	237.8
pyridine	260.6	255.6	255.6	252.9	247.7	241.2
tetrachloroethylene	219.5	215.9	216.3	215.5	209.9	205.5
	240.2[a]	236.4[a]	236.4[a]	230.9[a]	228.3[a]	219.9[a]
carbon tetrachloride	220.3	216.7	217.1	216.3	212.1	208.0
	236.4[a]	234.6[a]	233.6[a]	235.5[a]	230.0[a]	223.2[a]
trichloroethylene	232.3	227.9	228.3	227.4	221.1	215.2
chlorobenzene	244.6	240.7	240.7	238.3	234.1	227.9
o-dichlorobenzene	247.7	242.6	243.1	240.7	235.0	227.9
chloroform	244.1	238.8	239.7	238.3	231.4	224.0
methylene chloride	250.5	250.3	248.7	249.2	240.7	233.2
1,2-dichloroethane	250.5	250.3	249.7	248.2	241.2	234.6
2-methyl-2-propanol[b]	246.6	239.2	240.2	236.4	229.2	229.2
cyclohexanol	247.7	243.1	242.6	236.4	235.0	233.6
3-phenyl-1-propanol	252.9	247.2	247.7	255.6	240.7	235.5
2-propanol	248.7	244.6	243.6	239.2	235.5	233.2
1-pentanol	243.6	238.3	240.2	241.2	230.5	230.5
1-butanol	246.1	241.2	240.7	237.3	236.6	232.7
benzyl alcohol	258.4	252.9	252.9	248.7	245.6	240.7
ethanol	251.8	245.6	246.6	244.1	238.3	235.9
methanol	259.0	253.4	253.4	250.3	246.1	242.2

[a] Higher energy component observed as a shoulder. [b] Data recorded at 303 K.

further investigated. In previously published correlations of $M(CO)_4$(diimine) complexes with E_T or π^*, Connor and Overton have not segregated the solvents,[20] whereas Burgess et al. have grouped solvents into hydroxylic and nonhydroxylic classes.[6e] Kamlet and Taft's solvent polarity scale (π^*) incorporates correction factors segregating the nonhydroxylic solvents into nonchlorinated aliphatic, polychlorinated aliphatic, and aromatic classes.[11]

The large electronic influence of substituent is immediately seen from the colors of these complexes. For example, in benzene, $W(CO)_4$(4-Me-phen) appears red whereas $W(CO)_4(5\text{-}NO_2\text{-phen})$ is violet. The effects of varying ligand substituent on the MLCT absorption maxima are shown in Table II. For any particular solvent, the MLCT transition moves to lower energy with an increasing electron-withdrawing group on phen. Plots of E_{MLCT} vs. Hammett's para-substituent parameter (σ_p)[12] are shown for $M(CO)_4L$ in pyridine (slope -16.11 kJ mol^{-1}, correlation coefficient 0.968), ethanol (slope -11.73 kJ mol^{-1}, correlation coefficient 0.939), diethyl ether (slope -11.37 kJ mol^{-1}, correlation coefficient 0.970), and trichloroethylene (slope -15.01 kJ mol^{-1}, correlation coefficient 0.972) in Figure 3. These results indicate that the electron-withdrawing nature of the ligand substituent significantly affects the MLCT excited-state energy, and its influence is one that can be correlated to a high degree. Recently, the electronic effects of the ligand substituent have been reported to correlate with Hammett parameters for a series of $Mo(CO)_4$(4-4′-disubstituted-2,2′-bpy) complexes.[20]

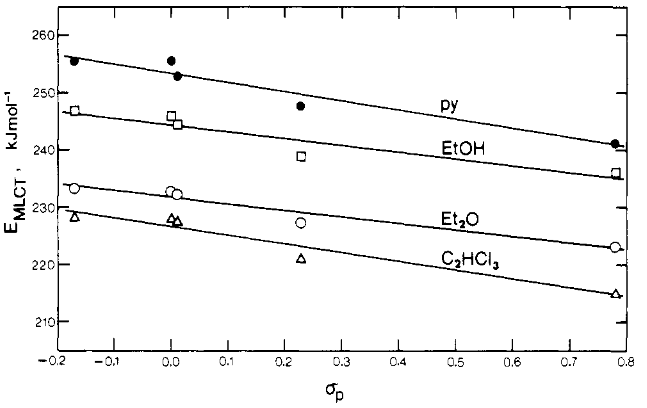

Figure 3. Energies of the MLCT (E_{MLCT}) of $W(CO)_4$(5-R-phen) in pyridine, ethanol, diethyl ether, and trichloroethylene plotted against σ_p substituent values. E_{MLCT} values are taken from Table II.

The solvent parameters E_T and π^* are derived from the molar transition energy of pyridinium *N*-phenolbetaine[10a] and the π–π^* solvent-induced transitions in a series of organic dyes, respectively. We define here a new solvent polarity scale based on the $M(CO)_4$(diimine) complexes:

$$E^*_{MLCT} = \frac{E_{MLCT} - E^0_{MLCT}}{E^1_{MLCT} - E^0_{MLCT}} \qquad (1)$$

This equation uses the MLCT energies (kJ mol^{-1}) of $M(CO)_4L$ in solvent (E_{MLCT}), isooctane (E^0_{MLCT}), and dimethyl sulfoxide

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[20] Connor, J. A.; Overton, C. *Inorg. Chim. Acta* **1982**, *65*, L1.

Table III. Derived Solvent Parameters[a]

solvent	E^*_{MLCT}	solvent	E^*_{MLCT}
isooctane	0.00	3-phenyl-1-propanol	0.53
carbon tetrachloride	0.12	1-butanol	0.55
tetrachloroethylene	0.13	tetrahydrofuran	0.59
triethylamine	0.23	1,2-dichloroethane	0.64
trichloroethylene	0.23	2-picoline	0.65
mesitylene	0.25	methylene chloride	0.67
toluene	0.30	benzyl alcohol	0.67
diethyl ether	0.32	cyclohexanone	0.69
benzene	0.34	ethanol	0.69
piperidine	0.41	3-pentanone	0.71
chloroform	0.42	methanol	0.73
1-pentanol	0.45	pyridine	0.77
chlorobenzene	0.46	acetone	0.82
2-propanol	0.46	dimethylacetamide	0.93
o-dichlorobenzene	0.48	dimethylformamide	0.95
cyclohexanol	0.49	acetonitrile	0.98
2-methyl-2-propanol	0.51	dimethyl sulfoxide	1.00

[a] From the data of $W(CO)_4bpy$.

(E^1_{MLCT}). The derived solvent parameter (E^*_{MLCT}) takes on values in an increasing polarity scale from 0 to 1. Values of E^*_{MLCT} for $W(CO)_4bpy$ are shown in Table III. The value of E^*_{MLCT} for acetonitrile has been added ($E_{MLCT} = 264.7$ kJ mol^{-1} for $W(CO)_4bpy$). The applicability of this solvent scale to other solvent-sensitive metal complexes was demonstrated by plotting E^*_{MLCT} vs. previously reported MLCT absorption maxima of $(\eta^5\text{-}C_5H_5)M(CO)_2py$ complexes (M = Mn and Re).[21] The least-squares regressions for the Mn (slope 34.52 kJ mol^{-1}, correlation coefficient 0.962) and Re (slope 42.13 kJ mol^{-1}, correlation coefficient 0.991) complexes indicate excellent fits; the E^*_{MLCT} solvent scale appears to be a good one for the low-lying MLCT states of transition-metal complexes. The E^*_{MLCT} scale could be used to estimate the position of a MLCT transition hidden by overlapping absorption bands, a situation often encountered in interpreting UV-visible spectra.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. $Cr(CO)_4bpy$, 15668-63-0; $Mo(CO)_4bpy$, 15668-64-1; $W(CO)_4bpy$, 15668-66-3; $W(CO)_4$(4-Me-phen), 87655-71-8; $W(CO)_4phen$, 14729-20-5; $W(CO)_4$(5-Me-phen), 59136-52-6; $W(CO)_4$(5-Ph-phen), 87655-72-9; $W(CO)_4$(5-Cl-phen), 59136-53-7; $W(CO)_4(5\text{-}NO_2\text{-phen})$, 87655-73-0.

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Complexation of $Zn(TPPS_3)$ by Methylviologen and Its Role in the Photoinduced Hydrogen Evolution with Hydrogenase

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Received April 14, 1983

As reported previously, water-soluble [*meso*-phenyltris(4-sulfonatophenyl)porphyrinato]zinc ($Zn(TPPS_3)$) has been found to be a suitable photosensitizer[1,2] for the photoinduced hydrogen evolution system containing a photosensitizer, an electron donor, an electron acceptor, and a suitable catalyst. Recently the complex formations between methylviologen and metalloporphyrins have been reported,[3-5] but the role of the complex formation in photoredox reactions has not been clarified yet. In this paper, we hope to describe the complex formation between $Zn(TPPS_3)$ and methylviologen and to discuss its role in photoredox processes.

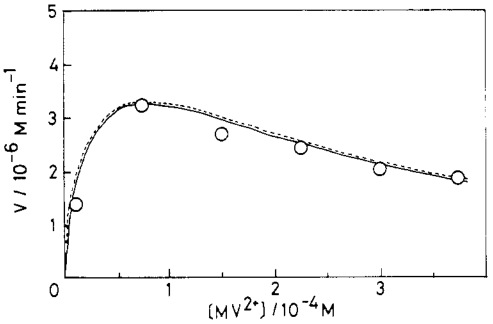

Figure 1. Relation between initial reduction rate of methylviologen and methylviologen concentration ($[Zn(TPPS_3)] = 8.33 \times 10^{-8}$ mol·dm^{-3}; [RSH] = 0.21 mol·dm^{-3}; reaction temperature 30 °C). The dotted line indicates a theoretical result.

As the reduced form of methylviologen (MV^+) has been known to produce hydrogen in the presence of a suitable catalyst, an attempt was also made to produce hydrogen by the use of an electron-transfer method that combines the $Zn(TPPS_3)$ and methylviologen photoirradiation system and hydrogenase, for hydrogenase is known as a specific enzyme for methylviologen.

Experimental Section

Methylviologen was purchased from Tokyo Kasei Kogyo Co., and the other chemicals, obtained from Wako Pure Chemical Co., were of the highest available purity. $Zn(TPPS_3)$ was synthesized by refluxing $TPPS_3$ and zinc acetate (molar ratio 1:10) in methanol for 2 h. Hydrogenase from Desulfovibrio vulgaris (Miyazaki type) was purified according to Yagi's method.[6]

The sample solution, which consisted of photosensitizer, methylviologen, 2-mercaptoethanol (RSH), and hydrogenase (if included), was deaerated by repeated freeze-pump-thaw cycles. A typical experiment was performed as follows under anaerobic conditions. To 5.00×10^{-10} mol of $Zn(TPPS_3)$, 7.56×10^{-7} mol of methylviologen, and 1.26×10^{-3} mol of RSH was added 1 mL of hydrogenase (if included). The volume of the mixture was adjusted to 6.0 mL with 0.02 mol·dm^{-3} of Tris-HCl buffer (pH 7.0). In the photolysis with continuous irradiation, the sample in a Pyrex cell with a magnetic stirrer was irradiated with light from a 200-W tungsten lamp (from a slide projector). The sample solution settled at distance 7 cm from the light source. Light of wavelength less than 390 nm was cut off by a Toshiba L-39 filter.

Results and Discussion

When an aqueous solution containing $Zn(TPPS_3)$, methylviologen, and RSH was irradiated, the growth of the cation radical of methylviologen, which has characteristic absorption bands at 395 and 605 nm, was observed. The formation rate of reduced methylviologen (MV^+) increased with methylviologen concentration and then decreased through a maximum point as shown in Figure 1. This abnormal phenomenon may imply the complexation of $Zn(TPPS_3)$ by methylviologen. When $Zn(TPPS_3)$ was mixed with methylviologen, the characteristic Soret absorption band (418 nm) decreased with the

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0020-1669/83/1322-3828$01.50/0