Table IV. Overlaps, Populations, and Energies for $PtCl_4^{2-}(\eta^1$- and η^2-$H_2)$[a]

	η^1	η^2
	Geometry	
$d(Pt-H_2)$	2.95	2.82
$d(H-H)$	0.89^b	0.89^b
	Overlaps	
$\langle 1\sigma_u \vert 3a_{1g}\rangle$	0.22	
$\langle 1\sigma_u \vert 2e_{1g}\text{-}x\rangle$		0.05
$\langle 1\sigma_g \vert 3a_{1g}\rangle$	0.09^5	0.16
	Populations (e)	
$P(1\sigma_u)$	0.08	0.02
$P(1\sigma_g)$	1.99	2.01
$P(3a_{1g})$	1.97	2.01
$P(2e_{1g}\text{-}x)$	2.00	1.99
	Energies (eV)	
ΔE_σ	−0.23	−0.19
ΔE_π	-0.07^5	−0.07
ΔE_{rest}	−0.05	−0.06
$\Delta E_{oi}{}^c$	−0.36	−0.31
ΔE°	+0.00	$+0.25^5$
$\Delta E(H\leftrightarrow H)$	+0.16	+0.16
ΔE_{tot}	−0.19	+0.10

[a] See Table I for explanation of the entries. [b] The H−H distances have not been optimized. [c] oi = orbital interaction.

The interaction of H_2 with $PtCl_4^{2-}$ is very weak, as expected: −0.19 eV in the η^1 mode and +0.10 eV in the η^2 mode (Table IV). The overlap of the d_σ ($3a_{1g}$) with H_2 σ^* is a sizable 0.22 in the η^1 mode, but the high energy of σ^* prevents strong σ bonding: $\Delta E_\sigma = -0.23$ eV, and $P(\sigma^*) = 0.08$ e. In η^2 mode the σ^* could act as π-acceptor orbital, but the overlap of σ^* with $2e_{1g}$ is small (0.05). As there are no nodes in the σ^* (except for the central plane of course), this small overlap must be caused by the different phases of $2e_{1g}$ on Pt and Cl. Although the $Cr(CO)_5-F_2$ example above shows that the mere presence of the nodal planes in the $3\sigma_u$ of η^2-F_2 is sufficient to cause a small overlap with a metal fragment orbital, the case of $PtCl_4^{2-}-H_2$ shows that also nodes in the metal fragment orbital prevent the building up of a large overlap. The small overlap and the high energy of the H_2 σ^* orbital result in a π bond that is quite weak (−0.07 eV). The occupied $1\sigma_g$ of H_2 has a four-electron destabilizing interaction (steric repulsion) with the $PtCl_4^{2-}$ $3a_{1g}$, which cancels in η^2 coordination (larger $1\sigma_g-3a_{1g}$ overlap) much of the bonding contributions. In conclusion, H_2 bonds preferentially in η^1 mode to $PtCl_4^{2-}$, as F_2 does, but rather weakly.

Summarizing, we have found the nodal structure of both the F_2 acceptor orbital $3\sigma_u$ (antibonding $p_\sigma-p_\sigma$) and the metal fragment donor orbital $2e_{1g}$ (antibonding $5d_\pi$−Cl 3p) to be responsible for the lack of π bonding in η^2 coordination and therefore for the preference of end-on over side-on coordination of F_2 to $PtCl_4^{2-}$. On the other hand, we have found the extended nature of the $8a_1$ (bonding dsp hybrid + CO π^*) an important factor for the preference of side-on coordination of H_2 to $Cr(CO)_5$. The opposite effects we have found here for on the one hand the π^* orbitals of the CO ligands in $Cr(CO)_5$, combining in a bonding fashion with the metal $3d_\pi$, and on the other hand the $3p_\pi$ orbitals of the Cl ligands in $PtCl_4^{2-}$, combining in an antibonding fashion with the metal $5d_\pi$, once more highlight the important role of ligands in tailoring metal d AOs for particular interactions. It is interesting to note that the η^1-coordinated $PtCl_4^{2-}-F_2$ provides a clear example of a metal–ligand bond that derives its strength from *σ back-donation* from metal to ligand.

Acknowledgment. We wish to thank Prof. G. van Koten for stimulating our interest in the subject of this investigation. The help of P. Vernooijs with the calculations and figures is also gratefully acknowledged.

Registry No. F_2, 7782-41-4; $PtCl_4^{2-}$, 13965-91-8; H_2, 1333-74-0; $Cr(CO)_5$, 26319-33-5.

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Photoreduction of Methylviologen Catalyzed by Phthalocyanine Complexes of Yttrium(III) and Lanthanoid(III) Metals

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Photoinduced hydrogen evolution from water has received considerable attention for the storage of solar energy and its conversion into a chemical form. Metal complexes such as $[Ru(bpy)_3]^{2+}$ and metallotetraphenylporphyrin have been used as photosensitizers.[1,2] It is one of the most important points that visible light can be used in the conversion of solar energy. In this regard, metallophthalocyanines, which show strong absorption bands in the wavelength region from 600 to 700 nm, are attractive candidates for the photosensitizer. Water-soluble phthalocyanine and its magnesium(II) or zinc(II) complex were examined as photosensitizers.[3] Phthalocyanine complexes of magnesium(II), aluminum(III), zinc(II), and cadmium(II) were also employed as the photosensitizer in a solvent mixture of DMF and water.[4] It was further reported that those metal complexes with tetra-2,3-pyridinoporphyrazine showed photoredox activities in the solvent.[5]

We previously reported that a sandwich-type PcLnPcH complex (Pc denotes the phthalocyanine dianion) was oxidized to a radical PcLnṖc species upon irradiation at λ > 320 nm in a solvent mixture of dichloromethane and acetonitrile.[6] Although the solubility of metallophthalocyanine complexes is usually very poor, a PcLnX complex (X denotes a monoanion) dissolves in common organic solvents such as methanol, acetone, or acetonitrile and also forms a relatively stable radical species depending upon the kind of X anions.[7] Thus, the lanthanoid(III) phthalocyanine complex, PcLnX, might be anticipated as a potential sensitizer for the photoredox system. In this paper, we report that the PcLnAcO complex (AcO denotes acetate anion) acts as the sensitizer for the photoreduction of methylviologen chloride ($MVCl_2$) in a methanol solution upon irradiation with visible light.

Experimental Section

Materials. The PcLnAcO complexes (Ln = Y(III), Sm(III), Gd(III), Yb(III), Lu(III)) were prepared according to the method described before:[8] the mixture of lanthanoid(III) acetate and phthalonitrile (1:8 mole ratio) was melted above 150 °C and was further heated at 200–230 °C for 2 h. The crude products (PcLnAcO, PcLnPcH, and decomposed organic compounds) were dissolved in DMF, and then the solution was poured on a silica gel column. The dark brown decomposed compounds accompanied by the PcLnPcH complex were at first eluted with methanol, following the blue PcLnAcO complex. The objective complex was obtained by concentration of the eluent and was confirmed by means of visible spectra and elemental analyses. $MVCl_2$ (Tokyo Kasei, reagent grade) and triethanolamine (TEOA) were used without further purification.

Apparatus. For steady-state irradiation, the sample solution in a glass cell with a 1-cm light path length was purged by argon gas and was irradiated with a 300-W tungsten lamp at 25 °C (the cell was situated 3 cm away from the light). The light with wavelength shorter than 440 nm was cut off by the use of a Toshiba Y-44 glass filter. The visible and fluorescence spectra were recorded on a Hitachi 200-20 spectrophotometer and a Hitachi 850 fluorescence spectrophotometer, respectively. Laser photolysis was carried out by using the second harmonics (532 nm, 100 ms) of a Quantel YG 580 Nd-YAG Q-switched laser. The details of the apparatus have been described elsewhere.[9]

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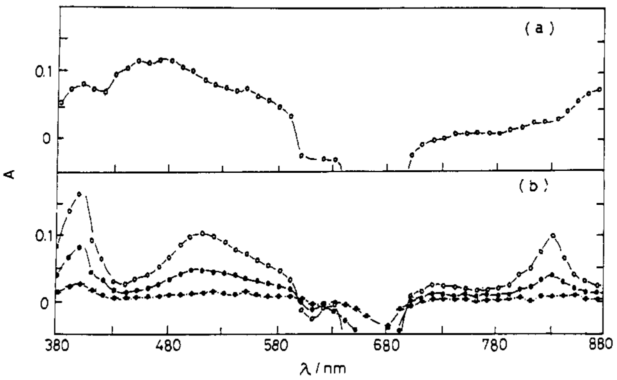

Figure 1. Transient difference absorption spectra after excitation at 532 nm in methanol: (a) the PcYAcO complex (6.00×10^{-6} M) 200 ns after excitation; (b) the two-component system of the complex (6.00×10^{-6} M) and $MVCl_2$ (3.00×10^{-4} M) (○) 7 μs, (●) 102 μs, and (⊖) 402 μs after excitation.

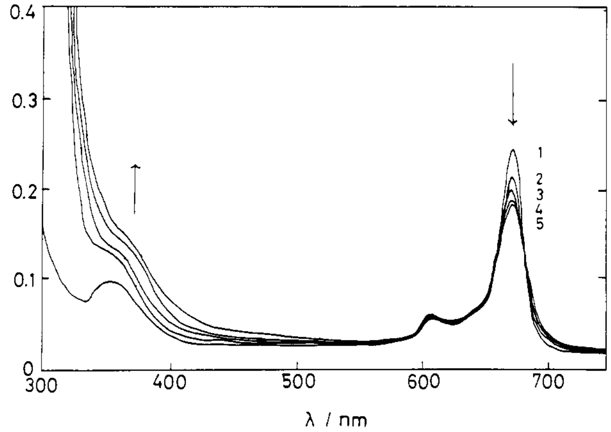

Figure 2. Spectral changes of the PcYAcO complex by the addition of $MVCl_2$ in methanol. [PcYAcO] = 3.50×10^{-6} M; [$MVCl_2$] = (1) 0, (2) 2.40×10^{-4}, (3) 4.80×10^{-4}, (4) 9.60×10^{-4}, and (5) 2.40×10^{-3} M.

Results and Discussion

The characteristic absorption bands of a radical $MV^{\bullet+}$ species appeared upon irradiation with visible light of the purged methanol solution containing TEOA (1.00×10^{-1} M), $MVCl_2$ (1.00×10^{-3} M), PcYAcO (3.00×10^{-6} M). The radical $MV^{\bullet+}$ species concentration generated upon irradiation for 40 min was estimated to be 57 times that of the complex. Without the complex, the radical cation was not generated under irradiation. When air was introduced into the irradiated sample solution in order to oxidize the $MV^{\bullet+}$ radical, the visible spectrum of the system became identical with that before irradiation. That is, in the course of the photoreduction, the complex effectively catalyzed the reaction.

In order to verify the quenching process, laser flash-photolysis experiments were carried out. A transient difference absorption spectrum of the PcYAcO complex is shown in Figure 1a, which is in good agreement with *T–T* absorption spectra of metal complexes reported (Mg,[4d,e] Zn,[4b,c] Al,[4c] In[4c,d]), while the life time of the transient is much shorter (1.6 μs) than those of the other metal complexes. Transient difference absorption spectra of the two-component system of the complex and $MVCl_2$ (3.00×10^{-4} M) are also shown in Figure 1b. The spectrum 7 μs after 532-nm excitation shows the formation of the $MV^{\bullet+}$ and $PcYAcO^{\bullet+}$ radicals; the strong band at 400 nm is ascribed to $MV^{\bullet+}$,[10] and the bands at 510, 720, and 830 nm are ascribed to $PcYAcO^{\bullet+}$.[4b,d,e] A strong negative absorption around 670 nm is attributable to the transient bleaching of the PcYAcO complex. These results clearly proved that the $PcYAcO^{\bullet+}$ radical is certainly formed in the quenching of ^{*3}PcYAcO by $MVCl_2$. Addition of $MVCl_2$ (0.25×10^{-3}–1.25×10^{-3} M) resulted in the faster decay of the excited triplet state, and $MV^{\bullet+}$ was produced with the same rate constant (4.5×10^9 M^{-1} s^{-1}) as the quenching rate constant of ^{*3}PcYAcO.

$$^{*3}\mathrm{PcYAcO} + \mathrm{MV}^{2+} \xrightarrow{k_q} \mathrm{PcYAcO}^{\bullet+} + \mathrm{MV}^{\bullet+} \qquad (1)$$

The absorbance of the PcYAcO complex at 670 nm decreased upon addition of $MVCl_2$ with isosbestic points at 652 and 681 nm, and the absorbance around 350 nm slightly increased, which is attributable to the adduct formation between the PcYAcO complex and $MVCl_2$ (Figure 2). Formation of the ground-state adduct was observed for all metallophthalocyanines examined here, and the formation constants (*K*) were obtained from the absorbance change at 670 nm (25 °C): $\log K = 2.78$ (4) for Y; 2.80 (2) for Sm; 2.71 (4) for Gd; 2.72 (5) for Yb; 2.84 (7) for Lu. The values obtained are little dependent upon the kinds of the central metal ions.

Addition of water (10% v/v) into the methanol solution of the three-component system (TEOA, $MVCl_2$, and PcYAcO) increased the association constant ($\log K = 2.93$) but decreased the relative quantum yield (RQY) of the $MV^{\bullet+}$ radical (0.82).[11] That is, the adduct formation suppresses the photoreduction of $MVCl_2$. This might be interpreted by the reason that the excited sensitizer is quenched in the S state in the adduct and prohibits the formation of the long-lived triplet state.[3b,3d]

Effects of the concentration of $MVCl_2$ on the RQY were also studied; RQY = 1.00 for [$MVCl_2$] = 5.00×10^{-4} M, 0.96 for 1.00×10^{-3} M, 0.75 for 5.00×10^{-3} M, and 0.58 for 1.00×10^{-2} M ([PcYAcO] = 3.50×10^{-6} M). This might result from the decrease of the free-type complexes by the adduct formation.

On the basis of these observations with the fact that the photoreduction by the metallophthalocyanine complexes proceeds via an oxidative process,[2b,4e] the following reaction scheme for the primary process might be proposed:

$$\mathrm{PcYAcO} + \mathrm{MV}^{2+} \overset{K}{\rightleftharpoons} [\mathrm{PcYAcO}\text{- - -}\mathrm{MV}^{2+}] \qquad (2)$$

$$\mathrm{PcYAcO} \xrightarrow{h\nu} {}^{*1}\mathrm{PcYAcO} \qquad (3)$$

$$^{*1}\mathrm{PcYAcO} \rightarrow {}^{*3}\mathrm{PcYAcO} \qquad (4)$$

$$^{*3}\mathrm{PcYAcO} \rightarrow \mathrm{PcYAcO} \qquad (5)$$

$$^{*3}\mathrm{PcYAcO} + \mathrm{MV}^{2+} \xrightarrow{k_q} \mathrm{PcYAcO}^{\bullet+} + \mathrm{MV}^{\bullet+} \qquad (1)$$

$$\mathrm{PcYAcO}^{\bullet+} + \mathrm{TEOA} \rightarrow \mathrm{PcYAcO} + \mathrm{TEOA}^{\bullet+} \qquad (6)$$

Fluorescence spectra of the lanthanoid(III) complexes were measured to elucidate the effect of the central metal ions. The

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relative fluorescence intensities are as follows: Y, 1.00; Sm, 0.10; Gd, 0.11; Yb, 0.06; Lu, 0.09.[12] This tendency might result from an inner heavy atom effect.

The RQY of the $MV^{\bullet +}$ radical was affected by the kinds of the central metal ions as follows: Y, 1.00; Sm, 0.50; Gd, 0.44; Yb, 0.22; Lu, 0.79.[13] As described above, the intersystem crossing is facilely performed by spin–orbit coupling on the central metal ion. However, in the case of the Sm(III), Gd(III), or Yb(III) ion, the energy transfer from the excited triplet state of the phthalocyanine ring to the excited state of the metal center might occur probably due to the lower energy levels (<5000 cm^{-1}) of f orbitals in the metal compared with that (ca. 8000 cm^{-1}) of the excited triplet state of the phthalocyanine,[14,15] resulting in the decrease of the quantum yield.

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(11) The relative quantum yield is estimated as a value relative to that in methanol. Those for the effects of $MVCl_2$ concentrations and central metal ions are also estimated as values relative to the largest one in the series, respectively.

(12) The fluorescence intensities at 674 nm are estimated as values relative to the largest one of the PcYAcO complex. If the intensity of the PcYAcO complex is compared with that of the PcZn complex (its fluorescence quantum yield in Me_2SO is 0.3),[4b] the quantum yield of the PcYAcO complex was estimated to be 0.15 in Me_2SO.

(13) To compare the quantum yield for the PcYAcO complex with that for the well-characterized PcZn complex,[4b] the RQY for the PcYAcO complex relative to that for the PcZn complex was measured to be 0.16 in the solvent mixture of Me_2SO and H_2O (9:1 v/v).

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Additions and Corrections

1989, Volume 28

R. Gerald Keil,* David W. Johnson, Mark A. Fryling, and James F. O'Brien: Investigation of Lithium–Water Interactions in Acetonitrile Solutions Using Proton Nuclear Magnetic Resonance, Raman, and Infrared Spectroscopies and Extended Hückel Molecular Orbital Calculations.

Page 2766. In the Molecular Orbital Calculations section, line 11 should read "is due to the σ-bonding interaction." Lines 14 and 15 should read "where the σ-donor orbital is slightly bonding."—R. Gerald Keil

Novelette Sadler, Susannah L. Scott, Andreja Bakac,* James H. Espenson,* and M. S. Ram: Effect of Steric Crowding on the Rates of Reactions of a Nickel(I) Tetraaza Macrocycle with Organic Halides and Hydroperoxides.

Page 3952. The caption to Figure 1 should read as follows: Structural formulas of (a) Ni(dmc) and (b) *R*,*S*,*R*,*S*-Ni(tmc).—Andreja Bakac