Bull. Chem. Soc. Jpn., ***68***, *178—182(1995)*

Photochemistry of μ-Amido-μ-hyperoxo-dicobalt(III) Complexes with Ammine and Polyamine Ligands in Aqueous Solutions: Effects of Ligand and pH

Nobuyoshi Shinohara,* Hirohiko Shibukawa, Kazuteru Shinozaki, and Mika Yoshikai

Department of Chemistry, Yokohama City University, Seto, Kanazawa-ku, Yokohama 236

(Received June 1, 1994)

Photolyses of μ-amido-μ-hyperoxo-dicobalt(III) complexes, $[\mathrm{LCo(NH_2,O_2{}^-)CoL}]^{4+}$ ($\mathrm{L{=}4NH_3}$ (**1**), en+ $\mathrm{2NH_3}$ (**2**), 2en (**3**), tren (**4**)), (tren: 2,2′,2″-triaminotriethylamine, en: ethylenediamine) were investigated. The photolysis of complex **4** in a neutral aqueous solution produced a μ-hydroxo-μ-peroxo-dicobalt(III) complex, $[\mathrm{(tren)Co(OH,O_2{}^{2-})Co(tren)}]^{3+}$, together with a mononuclear cobalt(III) complex, $[\mathrm{Co(NH_3)(tren)(H_2O)}]^{3+}$. A mononuclear complex and Co^{2+} were produced in the photolyses of μ-hyperoxo complexes **1** and **2** containing $\mathrm{NH_3}$ ligand in neutral aqueous solutions. In acidic media, only mononuclear complex and Co^{2+} were produced in the photolysis of all μ-hyperoxo complexes examined. Quantum yields of the complexes with $\mathrm{NH_3}$ increased with increasing the number of coordinated $\mathrm{NH_3}$ ($\phi{=}0.25$, 0.11, 0.023, and 0.028 for complexes **1**, **2**, **3**, and **4**, respectively, at 365 nm irradiation in neutral region). The quantum yields obtained in acidic solutions were similar in magnitude to those obtained in neutral solutions.

In the search for the catalysts capable of activating dioxygen for homogeneous oxidations under mild conditions, cobalt(II) chelates have attracted perhaps the most attention. Their catalytic activity often involves the formation of cobalt-dioxygen adducts formulated as peroxo or hyperoxo complexes. The photochemical behaviors of these complexes are very interesting; Hyperoxo cobalt(III) complexes are formed upon irradiation of oxygenated aqueous solutions of cobalt(III)-polyamine complexes,[1,2] and hyperoxo and μ-hyperoxo cobalt(III) complexes with ammine or polyamine ligand are recognized to be very photoactive.[3—5]

Photochemical reactions of μ-hyperoxo-dicobalt(III) complexes **1** and **3** in acidic aqueous solutions were studied, and the stoichiometry of the reactions was established:[5]

$$[\mathrm{LCo(NH_2,O_2{}^-)CoL}]^{4+} \xrightarrow[\mathrm{H^+,H_2O}]{h\nu} [\mathrm{Co(H_2O)(NH_3)L}]^{3+} + \mathrm{Co}^{2+} + \mathrm{L} + \mathrm{O_2}. \qquad (1)$$

We have found that μ-amido-μ-peroxo-dicobalt(III) complex, $[\mathrm{(en)_2Co(NH_2,\ O_2{}^{2-})Co(en)_2}]^{3+}$, is produced in the photolysis of complex **2** in a neutral aqueous solution (Eq. 2):[6]

$$\begin{aligned}2[\mathrm{(en)_2Co(NH_2,O_2{}^-)Co(en)_2}]^{4+} + 3\mathrm{H_2O} + \mathrm{H^+} &\xrightarrow{h\nu}\\ &[\mathrm{(en)_2Co(NH_2,O_2{}^{2-})Co(en)_2}]^{3+}\\ &+ cis\text{-}[\mathrm{Co(NH_3)(en)_2(H_2O)}]^{3+}\\ &+ cis\text{-}[\mathrm{Co(en)_2(H_2O)_2}]^{3+} + \mathrm{O_2} + \mathrm{H^+}, \qquad (2)\end{aligned}$$

where the acid ionization constants of *cis*-$[\mathrm{Co(NH_3)(en)_2(H_2O)}]^{3+}$ and *cis*-$[\mathrm{Co(en)_2(H_2O)_2}]^{3+}$ are $\mathrm{p}K{=}6.05$ (25 °C)[7] and $\mathrm{p}K_1{=}6.06$, $\mathrm{p}K_2{=}8.15$ (25 °C),[8] respectively.

This work has been extended to the photolysis of several other μ-amido-μ-hyperoxo-dicobalt(III) complexes: **1**, **2**, and **4** with ammine and/or other polyamine ligands. We have found that the photochemical decomposition products of the μ-hyperoxo-dicobalt(III) complexes differ with the kind of the coordinated ligand in the neutral region, but not in acidic solutions. The quantum yields of the photochemical decomposition of the μ-hyperoxo complexes also changed significantly due to the kind of ligand.

Experimental

Materials. $[\mathrm{(NH_3)_2(en)Co(NH_2,O_2{}^-)Co(en)(NH_3)_2}](\mathrm{NO_3})_4\cdot\mathrm{H_2O}$ (**2**) was prepared as follows: 1 g of $[\mathrm{(NH_3)_4Co(NH_2,O_2{}^-)Co(NH_3)_4}](\mathrm{NO_3})_4$ was treated with 0.22 g ethylenediamine dissolved in 4 ml water at about 50 °C until the smell of ammonia was weak. After the solution was cooled to room temperature, 2 ml of 2 M (1 M=1 $\mathrm{mol\,dm^{-3}}$) nitric acid solution containing 1 g $\mathrm{(NH_4)_2Ce\ (NO_3)_6}$ was added to the brown solution at ca. 25 °C and this mixture was left to stand for 30 min. A green complex salt, $[\mathrm{(NH_3)_2(en)Co(NH_2,O_2{}^-)Co(en)(NH_3)_2}](\mathrm{NO_3})_4\cdot\mathrm{H_2O}$, was precipitated by the addition of ethanol, filtered, and washed with ethanol and ether. The complex was recrystallized from 2 M nitric acid. The absorption spectrum of this complex has absorption maxima at 470 nm ($\log\varepsilon{=}2.62$) and 699 nm ($\log\varepsilon{=}2.53$), which were closely similar to those of related

μ-hyperoxo complexes.$^{9-11)}$ The Raman spectrum of the μ-hyperoxo complex showed a strong peak at 1042 cm^{-1} in the solid (excitation: 487.9 nm Ar^+ laser), assignable to ν(O–O).$^{11)}$ The structure of complex **2** was also supported by the fact that one of photodecomposition products of this complex was $[Co(NH_3)_3(en)(H_2O)]^{3+}$ as described later. Found: C, 8.02; H, 5.20; N, 28.93; Co, 19.05%. Calcd for $C_4H_{32}O_{15}N_{13}Co_2$: C, 7.85; H, 5.20; N, 29.36; Co, 19.01%.

$[(tren)Co(NH_2,O_2{}^-)Co(tren)](ClO_4)_4\cdot 2H_2O$$^{12)}$ (**4**) and $[(NH_3)_4Co(NH_2,O_2{}^-)Co(NH_3)_4]$ $(NO_3)_4$$^{13)}$ (**1**) were prepared using the methods in the literature. Authentic samples ($[(tren)Co(OH,O_2{}^{2-})Co(tren)](ClO_4)_3$ $\{\lambda_{max}=500$ (sh) $(\log\varepsilon=2.66)$, $\lambda_{max}=350$ $(\log\varepsilon=3.86)\}$,$^{12)}$ $[Co(NH_3)_3(en)(H_2O)](ClO_4)_3$ {fac; $\lambda_{max}=492.5$ $(\log\varepsilon=1.71)$, $\lambda_{max}=346.0$ $(\log\varepsilon=1.70)\}$,$^{14)}$ and $[Co(NH_3)(tren)(H_2O)](ClO_4)(NO_3)_2$ $\{\lambda_{max}=482$ $(\log\varepsilon=2.00)$, $\lambda_{max}=349$ $(\log\varepsilon=1.88)\}$$^{15)}$ were also prepared using the methods in the literature.

Photochemical Procedures. Sample solutions were irradiated in a quartz cell at room temperature, and the light sources comprised a high-pressure mercury lamp UM-102 (100 W) or a Xe-lamp UXL-500D (500 W) (Ushio Electric Co.). The first source was used to supply 313$^{16a)}$ and 365 nm$^{16b)}$ irradiation, which were obtained by a combination of solution and glass filters. The second source was used for 470 nm irradiation: The wavelength selection was effected by an interference filter with a transmittance maximum at 470 nm and fwhm of 15 nm and a glass UV cutoff filter (Toshiba Y-46). The incident light intensities were measured by potassium tris(oxalato)ferrate(III) actinometry.

Analytical Procedures. The absorption spectra were recorded on a Shimadzu UV-2100 spectrophotometer. The oxygen evolved by irradiation was measured polarographically with a Clarke-type electrode attached to a Yellow Springs Instruments O_2 meter as described previously.$^{17)}$ Separations of the products were carried out with a cation-exchange resin (CM-sephadex C-25 in the sodium form) described previously.$^{6)}$ The identification of the products was carried out by comparing the absorption spectra with those of synthesized authentic samples. Co^{2+} was determined spectrophotometrically by extracting Co(II) from aqueous solutions in methylisobutylketone in the presence of a large excess of thiocyanate ion.$^{18)}$

Results and Discussion

Photolysis. The absorption spectra of μ-amido-μ-hyperoxo-dicobalt(III) complexes, $[LCo(NH_2,O_2{}^-)CoL]^{4+}$, have absorption bands at ca. 300 ($\pi_h{}^*\rightarrow d\sigma$), ca. 350 (sh) ($\pi_v{}^*\rightarrow d\sigma$), ca. 470 (d→d), and ca. 700 nm ($d\pi\rightarrow\pi_h{}^*$).$^{19)}$ These complexes are known to be stable in acidic aqueous solutions. Valentine and Valentine, Jr.,$^{5)}$ reported that the complexes **1** and **3** decomposed photochemically very easily to give a mononuclear cobalt (III) complex and Co^{2+} in acidic aqueous solutions, according to Eq. 1.

Complexes **2** and **4** also decomposed very easily upon irradiation with near ultraviolet light ($O_2{}^-\rightarrow$Co(III) charge transfer bands). The absorption spectral changes upon irradiation of complex **4** in an acidic aqueous solution are shown in Fig. 1A. The two absorption peaks at 464 and 715 nm decreased with increasing irradiation time. The prolonged irradiation resulted in two new weak absorption bands at 340 and 490 nm, which were ascribed to $[Co(NH_3)(tren)(H_2O)]^{3+}$. Similar results were obtained for 365 and 436 nm irradiation. The photolysis of the complexes **2** and **4** formed a mononuclear cobalt(III) and Co^{2+} in an acidic solution (Table 1), and the stoichiometry observed in the decompositions was analogous to those observed with the complexes **1** and **3** in an acidic aqueous solution (Eq. 1).$^{5b,6)}$

Complex **1** is unstable in a neutral aqueous solution, while complex **2** is relatively stable; its absorption spectrum does not change for at least 40 min at room temperature. However, complex **2** decomposed very easily upon irradiation with near ultraviolet light, and the decomposition was accelerated by the increased pH of the solutions accompanied by the detachment of the coordinated NH_3.$^{20)}$ The complex reactions occur under these conditions; therefore, the decomposition reactions have been studied in acetate buffer solutions of pH=6 where the complexes **1** and **2** are stable. The photochemical decomposition of the complexes occurs uniformly in the buffer solution; the modes of the spectral changes are similar to that in Fig. 1A. The photolysis of complexes **1** and **2** in the buffer solution of pH=6 gave the same products as those in an acidic solution (Table 1). The results can be explained as follows: The dissociation of the coordinated NH_3 takes place very rapidly compared to that of the coordinated en.$^{20)}$

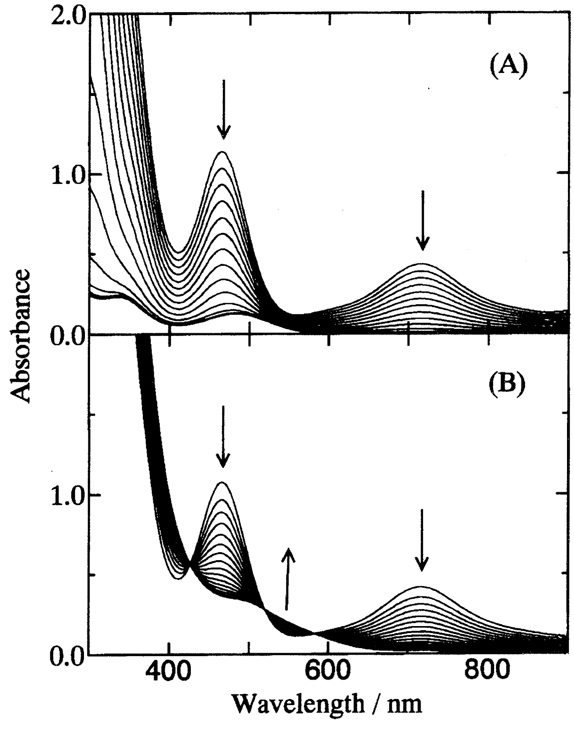

Fig. 1. Absorption spectral changes of 1.00×10^{-3} M $[(tren)Co(NH_2,O_2{}^-)Co\ (tren)]^{4+}$ aqueous solutions. Irradiated at 3 min intervals at 313 nm. A: in 0.1 M $HClO_4$ aqueous solution, B: in H_2O.

Table 1. Photochemical Decomposition Stoichiometries for $[LCo(NH_2,O_2^-)CoL]^{4+}$ Complexes[a)]

L	Acidity	Photochemical products				
		$[LCo(X, O_2^{2-})CoL^{3+}]$	$[CoL(NH_3)(H_2O)^{3+}]$	$[CoL(H_2O)_2^{3+}]$	$[Co^{2+}]$	$[O_2]$[b)]
		M ×10^3	M ×10^3	M ×10^3	M ×10^3	M ×10^3
$4NH_3$	pH=6.0[c)]		1.02		0.93	0.97
	0.1 M $HClO_4$		1.00[d)]		1.00[d)]	—
$2NH_3$+en	pH=6.0[c)]		0.99		0.87	1.01
	0.1 M $HClO_4$		0.99		0.95	1.01
2en	H_2O	0.46[e)]	0.53	0.40		0.49
	0.1 M $HClO_4$		1.00[f)]		1.00[f)]	1.00[f)]
tren	H_2O	0.47[g)]	0.95			0.49
	0.1 M $HClO_4$		0.95		1.01	0.96

a) Initial concentration of $[LCo(NH_2,O_2^-)CoL]^{4+}$ was 1.0×10^{-3} M and all of the μ-hyperoxo complexes were decomposed. b) The evolved oxygen was determined at the low concentration of 1.0×10^{-4} M $[LCo(NH_2,O_2^-)CoL]^{4+}$ ion in order to avoid generation of O_2 bubbles gas in the cell equipped with an electrode of O_2 meter because of its low solubility. The values given in the column were multiplied ten times. c) 0.1 M acetate buffer. d) Ref. 5b; The experiment was carried out at the concentration of 5.0×10^{-4} M $[LCo(NH_2,O_2^-)CoL]^{4+}$. Therefore, the values given in the column were multiplied two times. e) $X=NH_2^-$. f) Ref. 5a. g) $X=OH^-$.

Table 2. Quantum Yields in the Photolysis of $[LCo(\mu\text{-}NH_2,\mu\text{-}O_2^-)CoL]^{4+}$ Solutions

L	Medium	Excitation wavelenth/nm					
		313	320	350	365	405	470
$4NH_3$	pH=6.0[a)]	0.47			0.25		0.089
	0.1 M $HClO_4$	0.56	0.49[b)]	0.40[b)]	0.34	0.1[b)]	0.112
$2NH_3$+en	pH=6.0[a)]	0.22			0.11		0.044
	0.1 M $HClO_4$	0.27			0.12		0.042
2en	H_2O	0.073			0.023		0.005
	0.1 M $HClO_4$	0.070	0.065[c)]	0.040[c)]	0.022	0.005[f)]	0.004
tren	H_2O	0.093			0.028		0.009
	0.1 M $HClO_4$	0.094			0.029		0.006

a) 0.1 M acetate buffer solutions. b) Ref. 5b. c) Ref. 5a.

Therefore, the photoinduced $[Co(NH_3)_4(H_2O)_2]^{2+}$ or $[Co(en)(NH_3)_2(H_2O)_2]^{2+}$ will decompose to give Co^{2+} and free ligands without reacting with O_2.

The absorption spectrum changes of the complex **4** upon irradiation are given in Fig. 1B, which shows that three isosbestic points were maintained throughout the photolysis. The photochemical decomposition products are given in Table 1. Identification of the μ-peroxo-dicobalt(III) complex, $[(tren)Co(OH,O_2^{2-})Co(tren)]^{3+}$, as a product, from the μ-hyperoxo complex **4** rests on spectral investigation of the trivalent fractions isolated by ion-exchange chromatography of the photolyzed solutions: The absorption spectrum of $[(tren)Co(OH,O_2^{2-})Co(tren)]^{3+}$ (λ_{max}=350 nm) is very similar to that of $[(tren)Co(NH_2,O_2^{2-})Co(tren)]^{3+}$ (λ_{max}= 325 nm).[12)] However, there is some difference in wavelength between λ_{max}'s. The absorption spectrum of the isolated dicobalt(III) complex exhibited an absorption maximum at 347 nm, assignable to $[(tren)Co(OH, O_2^{2-})Co(tren)]^{3+}$. There results suggest the following reaction mechanism (Eqs. 1a, 3, and 4):

$$[(tren)Co(NH_2,O_2^-)Co(tren)]^{4+} \overset{h\nu}{\rightleftarrows} {}^*[(tren)Co(NH_2,O_2^-)Co(tren)]^{4+} \xrightarrow{H_2O} [Co(NH_3)(tren)(H_2O)]^{3+} + [Co(tren)(H_2O)_2]^{2+} + O_2 \quad (1a)$$

$$[Co(tren)(H_2O)_2]^{2+} + O_2 \rightarrow [Co(tren)(H_2O)O_2]^{2+} + H_2O \quad (3)$$

$$[Co(tren)(H_2O)O_2]^{2+} + [Co(tren)(H_2O)_2]^{2+} \rightarrow [(tren)Co(OH,O_2^{2-})Co(tren)]^{3+} + H_2O. \quad (4)$$

The photoproduced $[Co(tren)(H_2O)_2]^{2+}$ reacts with O_2 to give $[(tren)Co(OH, O_2^{2-})Co(tren)]^{3+}$ according to reactions 3 and 4 where the rate constant k_3 of reaction 3 is 2.8×10^3 $M^{-1}\,s^{-1}$.[21] This mechanism is also supported by $[Co(tren)(H_2O)_2]^{3+}$ not being detected, and the overall reaction is written as in Eq. 5:

$$\begin{aligned}&2[(tren)Co(NH_2,O_2{}^-)Co(tren)]^{4+}+3H_2O\\&\rightarrow[(tren)Co(OH,O_2{}^{2-})Co(tren)]^{3+}\\&+2[Co(NH_3)(tren)(H_2O)]^{3+}+O_2+OH^-.\end{aligned} \quad (5)$$

The photolysis of complex **2** forms μ-amido-μ-peroxo-dicobalt(III) complex $[(en)_2Co(NH_2,O_2{}^{2-})Co(en)_2]^{3+}$.[6] On the other hand, the photolysis of complex **4** in a neutral aqueous solution forms μ-hydroxo-μ-peroxo-dicobalt(III) complex $[(tren)Co(OH,O_2{}^{2-})Co(tren)]^{3+}$. These results suggest the following mechanisms: In the photolysis of complex **3**, the reaction of $[Co(en)_2(H_2O)_2]^{2+}$, photoproduced by a reaction similar to Eq. 1a, with the remaining μ-hyperoxo complex **3**, leads to the formation of $[Co(en)_2(H_2O)_2]^{3+}$ and $[(en)_2Co(NH_2, O_2{}^{2-})Co (en)_2]^{3+}$ (Eq. 1).[6] In the photolysis of complex **4**, the reaction of $[Co(tren)(H_2O)_2]^{2+}$ with O_2 precedes the reaction of that with the remaining μ-hyperoxo complex **4**. The difference in the decomposition mechanisms will be attributed to the difference of the ease of the oxygenation of photoinduced $[Co(en)_2(H_2O)_2]^{2+}$ and $[Co(tren)(H_2O)_2]^{2+}$. These mechanisms are supported by the following facts: 1) Sasaki et al. reported that $[(en)_2Co(OH,O_2{}^{2-})Co(en)_2]^{3+}$ is formed from $[Co(en)_2(H_2O)_2]^{2+}$ and O_2 at pH>7.[22] Natarajan et al. also reported that flash photolysis of a series of Co(III)-amine complexes (for example; $[Co (en)_2(NO_2)_2]^{3+}$) in aerated aqueous solutions did not show any transient due to the oxygenation of the photoproduced Co(II)-amine.[23] 2) It was confirmed that $[(tren)Co(OH,O_2{}^{2-})Co(tren)]^{3+}$ was formed very rapidly even at pH≈6 by air-bubbling through a solution of 1:1 molar ratios of Co^{2+} and tren. The rate constant of the reaction of $[Co(tren)(H_2O)_2]^{2+}$ with O_2 was reported to be 2.8×10^3 $M^{-1}\,s^{-1}$.[21]

Quantum Yields. Quantum yields for the photochemical decomposition of the μ-amido-μ-hyperoxo-dicobalt(III) complexes are given in Table 2. If the ammonia are substituted by tren, the quantum yield for the μ-hyperoxo complexes dropped very markedly as in the case of the complex substituted by en. The quantum yield for the complex **2**, which has both NH_3 and en, lay between those of the complexes **1** and **3**.

The absorption band near 300 nm has been assigned to a charge transfer transition ($\pi_h{}^*\rightarrow d\sigma$) in which the electronic charge density is transferred from the oxygen to one of the cobalt(III) units. The photolysis at near-ultraviolet light occurs in the same manner but with a smaller quantum yield. The complexes, **1** and **2**, which have coordinated NH_3 groups, undergo efficient photochemical decompositions upon irradiation, and the principal photochemical reactivity of these complexes is associated with the absorption bands having maxima near 300 nm, which have been assigned to oxygen-to-cobalt electron transfer transitions. The quantum yields for all complexes investigated are the same essentially in acidic and neutral solutions.

We thanks Dr. H. Sugiura for his measurement of Raman spectra of complexes.

References

1) N. Shinohara, K. Ishii, and M. Hirose, *J. Chem. Soc., Chem. Commun.*, **1990**, 700.

2) A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, **112**, 2273 (1990).

3) H. R. Macke and A. F. Williams, "Photoinduced Electron Transfer," ed by M. A. Fox and M. Chanon, Elsevier, Amsterdam (1988), "Part D, Photoinduced Electron Transfer Reactions: Inorganic Substrates and Applications," Chap. 5. 2.

4) A. G. Sykes, *Trans, Faraday Soc.*, **59**, 1325 (1963); J. E. Barness, J. Barrett, and J. Brown, *J. Inorg. Nucl. Chem.*, **30**, 2207 (1963).

5) a) J. S. Valentine and D. Valentine, Jr., *Inorg. Chem.*, **10**, 393 (1971); b) J. S. Valentine and D. Valentine, Jr., *J. Am. Chem. Soc.*, **93**, 1111 (1971); c) J. S. Valentine and D. Valentine, Jr., *Inorg. Chem.*, **12**, 1697 (1973).

6) N. Shinohara, E. Kose, and W. Ohkubo, *Bull. Chem. Soc. Jpn.*, **61**, 3338 (1988).

7) R. D. Cannon and J. E. Earley, *J. Am. Chem. Soc.*, **88**, 1872 (1966).

8) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

9) Y. Sasaki, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **26**, 3373 (1971).

10) K. Osafune and K. Kimura, *Chem. Phys. Lett.*, **25**, 47 (1973).

11) T. Shibahara, *J. Chem. Soc., Chem. Commun.*, **1973**, 864; T. B. Freedman, C. M. Yoshida, and T. M. Loehr, *J. Chem. Soc., Chem. Commun.*, **1974**, 1016; C. G. Barraclough, G. A. Lawrance, and P. A. Lay, *Inorg. Chem.*, **17**, 3317 (1978).

12) C. -H. L. Yang and M. W. Grief, *Inorg. Chem.*, **12**, 663 (1973).

13) M. Mori, J. A. Weil, and M. Ishiguro, *J. Am. Chem. Soc.*, **90**, 615 (1968).

14) F. Yajima, Y. Koike, T. Sakai, and S. Fujiwara, *Inorg. Chem.*, **11**, 2054 (1972).

15) D. A. Buckingham, I. I. Creaser, W. Marty, and A. M. Sargeson, *Inorg. Chem.*, **11**, 2738 (1972).

16) a) M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948); b) V. Balzani, V. Carassiti, L. Moggi, and F. Scandola, *Inorg. Chem.*, **4**, 1243 (1965).

17) N. Shinohara and Y. Nakamura, *Bull. Chem. Soc. Jpn.*, **62**, 734 (1989).

18) E. R. Kantrowitz, M. Z. Hoffman, and J. E. Endicott, *J. Phys. Chem.*, **75**, 1914 (1971).

19) A. B. P. Lever, *J. Mol. Struct.*, **59**, 123 (1980); A. B. P. Lever and H. B. Gray, *Acc. Chem. Res.*, **11**, 348 (1978).

20) N. Shinohara, H. Lilie, and M. G. Simic, *Inorg. Chem.*, **16**, 2809 (1977); M. Simic and J. Lilie, *J. Am. Chem. Soc.*, **96**, 291 (1974).

21) G. Mclendon and A. E. Martell, *J. Coord. Chem.*, **4**, 235 (1975).

22) Y. Sasaki, K. Z. Suzuki, A. Matsumoto, and K. Saito, *Inorg. Chem.*, **21**, 1825 (1982).

23) P. Ramamurthy and P. Natarajan, *Inorg. Chem.*, **25**, 3554 (1986).