60 and 80 K, the compound begins to decompose to form a new iron-containing species. At room temperature, a very stable, nonvolatile residue remains. The isomer shift of this complex is similar to that found for covalently bound tetragonal FeS ($\delta = +0.35$ mm/s at 300 K).[17,18] Crystalline FeS shows no quadrupole splitting, whereas this complex does. However, this may be explained by the fact that amorphous rather than tetragonal FeS should form under these circumstances. In the former, the Fe is in a less symmetrical environment than in the latter, so that a doublet is expected. The new peak or doublet seen in Figure 1b also has the same isomer shift as FeS at 20 K ($\delta \sim +0.5$ mm/s). The change in δ with temperature is due to the second-order Doppler effect. These observations suggest that $Fe(CS_2)$ dissociates to form FeS upon warming (eq 1).

$$\mathrm{Fe(CS_2)} \xrightarrow{\Delta} \mathrm{FeS} + \mathrm{CS}\ \text{(volatile, decomposes)} \qquad (1)$$

Several samples in which iron was cocondensed in dilute carbon disulfide matrices (0.1–10% in Ar) at 20 K were examined by infrared spectroscopy. Matrix-isolated $^{12}CS_2$ in Ar absorbs at 1535 cm^{-1} and natural-abundance $^{13}CS_2$ at 1475 cm^{-1} in the infrared spectrum. A large portion of the CS stretching region (i.e. from 800 to 1500 cm^{-1}) is transparent in the CS_2 matrices. However, no new bands that could be attributed to coordinated CS_2 were ever seen in any of the $Fe/CS_2/Ar$ experiments.

One possible explanation is that the CS stretching bands are too weak to be resolved by the infrared spectrophotometer used in the experiments. To test this hypothesis, an experiment in which nickel was cocondensed in a 1% CS_2/Kr matrix at 20 K was repeated using the same conditions that were used for the iron experiments. The reaction of nickel in low-temperature CS_2/Ar and CS_2/Kr matrices has been reported by Ozin et al.[17] New bands in the CS stretching region of the infrared spectrum were detected, which were assigned to several $Ni–CS_2$ compounds in which CS_2 is bound through both carbon and sulfur as in I. Under the conditions employed in this study, the spectra published by Ozin were reproduced, indicating that the CS stretching bands in the nickel complexes are easily detected. This suggests, but does not prove conclusively, that such peaks should be seen in the IR spectrum if $Fe(CS_2)$ has bonding similar to that seen in the nickel complexes.

Another possibility for the apparent lack of CS stretching bands in the infrared spectra of iron cocondensed with CS_2 in a CS_2/Ar matrix is that these bands coincide with the strong free-CS_2 stretch at about 1535 cm^{-1}. If CS_2 is bound to iron in a linear fashion through sulfur, as in II, the expected frequency of the CS stretching band is about 1520 cm^{-1}.[1] Such a peak would indeed be obscured by the broad band of matrix-isolated free CS_2.

Although Mössbauer results do not usually give any direct information about bonding or structure of compounds, the spectra obtained for this study do provide some clues, particularly when compared to results obtained on other matrix-isolated systems. These comparisons yield the following relevant information. First, there is evidence for only one iron–CS_2 compound, $Fe(CS_2)$, in all of the matrices, whereas, for nickel,[17] up to three CS_2 ligands can coordinate to give $Ni(CS_2)_x$ ($x = 1–3$). Second, the isomer shift for $Fe(CS_2)$ of +0.55 mm/s is similar to that found for $Fe(C_2H_4)$[18] (+0.55 mm/s) and $Fe(NH_3)$[19] (+0.60 mm/s) complexes in which σ-bonding predominates. Third, matrix isolation experiments in which iron is cocondensed with reactive gases show that multicoordinate complexes are formed when the ligands are π-acids as in CO,[11] N_2,[14] and NO.[20] If the ligands are poor π-acceptors, such as NH_3, only monocoordinate complexes are formed.[19] Interestingly, nickel will coordinate up to three ethylene ligands in a π-bound fashion[21] whereas iron coordinates only one,[18] and the bonding is primarily via σ-donation. The final piece of evidence is that $Fe(CS_2)$ decomposes upon heating to form FeS.

It is apparent, then, that $Fe(CS_2)$ is probably σ-bonded, as would be found in linearly coordinated CS_2 (II), in contrast to the case of the nickel compounds. This difference in behavior between iron and nickel with CS_2 is analogous to that seen with ethylene.

Finally, an important feature of the Fe/CS_2 experiments was the total absence of unreacted iron atoms even in matrices containing as little as 0.1% CS_2 in Kr. It is usual to find unreacted iron atoms in matrices such as pure CO.[11] This has been explained by the fact that energy needs to be supplied to iron atoms in the ground state, $(3d)^6(4s)^2$, in order to promote them to the $(3d)^7(4s)^1$ state. Apparently, the CS_2 reaction differs in that little or no activation energy is required, implying that the interaction may occur with atoms in the ground state. Whatever the explanation, this system is distinguished by the fact that it has been found to be the most reactive one involving matrix-isolated iron atoms to date. This is even more remarkable in light of the fact that there is no evidence for reaction products when iron is cocondensed with CO_2.[22]

Summary

It has been shown that the cocondensation of iron with CS_2 in low-temperature matrices leads to the formation of one complex with stoichiometry $Fe(CS_2)$. The evidence at hand strongly suggests that CS_2 is σ-bonded to Fe, probably through S in a linear geometry. The unusually high reactivity and the very different behaviors of Fe and Ni toward CS_2 are striking features of this system.

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Registry No. $Fe(CS_2)$, 102505-25-9; FeS, 1317-37-9; Fe, 7439-89-6; CS_2, 75-15-0.

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[17] Huber, H.; Ozin, G. A.; Power, W. J. *Inorg. Chem.* **1977**, *16*, 2234.

[18] Parker, S. F.; Peden, C. H. F.; Barrett, P. H.; Pearson, R. G. *Inorg. Chem.* **1983**, *22*, 2813.

[19] Barrett, P. H.; Pasternak, M. *J. Chem. Phys.* **1979**, *71*, 3837.

[20] Doeff, M. M.; Barrett, P. H.; Pearson, R. G. *Inorg. Chim. Acta*, in press.

[21] Huber, H.; Ozin, G. A.; Power, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 6508.

[22] Klee, C.; McNab, T. K.; Litterst, F. J.; Micklitz, H. *Z. Phys.* **1974**, *270*, 31.

Contribution from the Solar Energy Research Group,
The Institute of Physical and Chemical Research,
Wako, Saitama 351-01, Japan

Laser Photolysis Studies of Nickel(II) Tetraphenylporphyrin in a Mixed Solvent of Pyridine and Toluene in the Temperature Range 180–300 K

Mikio Hoshino

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Since chemical and physical properties of metalloporphyrins are markedly dependent on the nature of axial ligands, the studies on the binding of ligands by metalloporphyrins have been extensively carried out by optical absorption, ESR, and NMR measurements.[1-3] For nickel(II) porphyrins, it is confirmed that five- and six-coordinate complexes are produced in the presence of pyridine or piperidine.[4-6] The absorption spectra of the

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[1] Miller, J. R.; Dorough, G. D. *J. Am. Chem. Soc.* **1952**, *74*, 3977–3981.

[2] Walker, F. A. *J. Am. Chem. Soc.* **1970**, *92*, 4235–4243.

[3] La Mar, G. N.; Walker, F. A. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1979; Vol. IV, Chapter 2.

[4] Cole, S. J.; Curthoys, G. C.; Magnusson, E. A.; Phillips, J. N. *Inorg. Chem.* **1972**, *11*, 1024–1028.

[5] Walker, F. A.; Hui, E.; Walker, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 2390–2397.

[6] Caughey, W. S.; Deal, R. M.; Mclees, B. D.; Alben, J. D. *J. Am. Chem. Soc.* **1962**, *84*, 1735–1736.

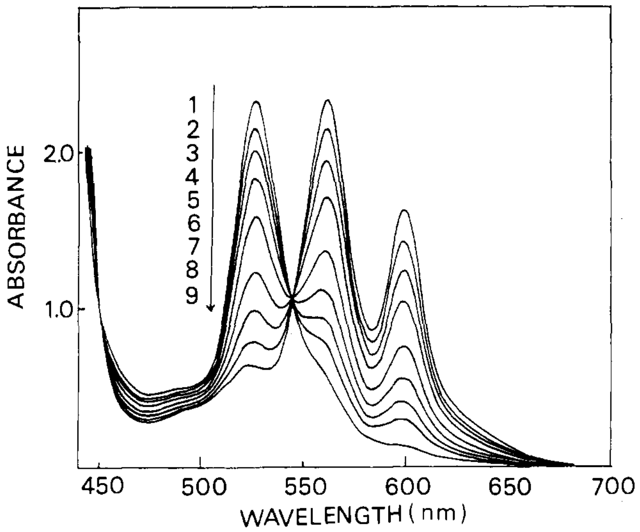

Figure 1. Absorption spectral changes observed for $Ni^{II}TPP$ in a mixed solvent of 2:3 pyridine and toluene: 1, at 297.7 K; 2, at 260.1 K; 3, at 250.3 K; 4, at 240.2 K; 5, at 230.2 K; 6, at 220.2 K; 7, at 210.2 K; 8, at 200.2 K; 9, at 180.3 K.

five-coordinate complexes are found to differ slightly from those of nickel(II) porphyrins free of axial ligand. The six-coordinate complexes, however, exhibit absorption spectra markedly different from those of nickel(II) porphyrins.[5] The NMR studies demonstrate that (1) the five-coordinate complexes have two spin states, $S = 0$ and $S = 1$, which are in thermal equilibrium each other, and (2) the six-coordinate complexes are solely in the $S = 1$ state.[3]

In comparison with the thermodynamic studies on the ligand-binding reactions, the photochemisty of nickel(II) porphyrins has received less attention. Recently, picosecond laser photolysis revealed that nickel(II) porphyrins in pyridine solutions undergo photoinduced ligand dissociation and association in the excited state at room temperature.[7,8] This paper reports the conventional laser photolysis studies of nickel(II) tetraphenylporphyrin, $Ni^{II}TPP$, in a mixed solvent of 2:3 pyridine and toluene over the temperature range 300–180 K.

Experimental Section

Purified $Ni^{II}TPP$ was kindly donated by Dr. K. Yamamoto of our institute. Reagent grade pyridine and benzene were used as supplied.

Optical absorption spectra were recorded on a Hitachi 330 spectrophotometer. Laser photolysis studies were carried out by using the second harmonics (530 nm) of a Nd:YAG laser from J. K. Lasers Ltd.: the pulse duration and energy were 20 ns and 100 mJ/pulse, respectively. The detection system for transient spectra has been reported elsewhere.[9] Temperatures of sample solutions were controlled by a cryostat from Oxford Instruments (Model DN 10200) with precision of ±1.0 °C.

Results and Discussion

Figure 1 shows the absorption spectral changes observed for $Ni^{II}TPP$ in the mixed solvent from 297.9 to 180.3 K. The spectrum measured at 297.9 K has a peak maximum at 527 nm and two absorption shoulders at 560 and 600 nm. The 527-nm peak decreases in intensity and new absorption peaks appear at 562 and 599 nm on going from 297.9 to 180.3 K. The spectral changes occurring below 180.3 K were found to be very small. The isosbestic points appearing in the spectral changes indicate that two species are in equilibrium in the temperature range studied.

Cole and his co-workers[4] have studied the thermodynamic functions for the addition of pyridines to nickel(II) porphyrins. They found that $Ni^{II}TPP$ in benzene reacts with a pyridine molecule to form a mono(pyridine) adduct: the equilibrium constant is obtained as 1360 M^{-1} at 298 K. Taking account of the high concentration of pyridine (4.9 M), we consider that the absorption spectrum observed at 297.7 K, as shown in Figure 1, is ascribed to the mono(pyridine) adduct of $Ni^{II}TPP$.

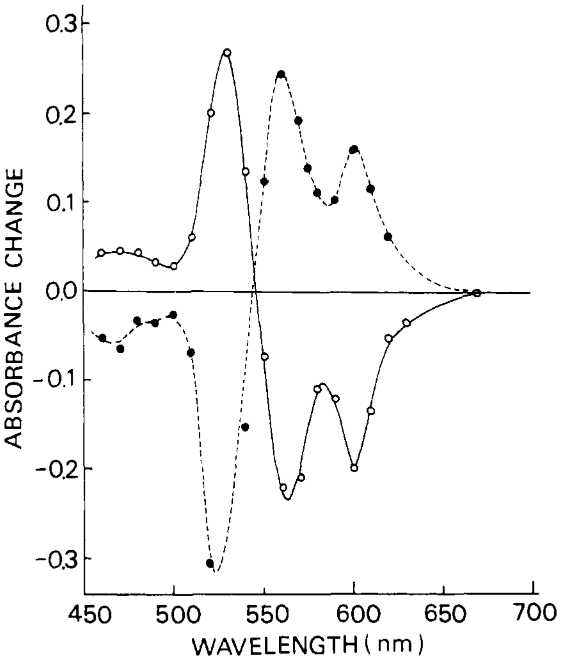

Figure 2. Transient absorption spectra observed for $Ni^{II}TPP$ in a mixed solvent of 2:3 pyridine and toluene at 20 ns after a laser pulse at 280.4 (●) and 181.2 K (○).

Walker and his co-workers[5] have studied the absorption spectral changes observed for $Ni^{II}TPP$ in toluene with the addition of piperidine. The spectrum of the bis(piperidine) adduct of $Ni^{II}TPP$ is in good accord with that observed at 180.3 K in this study. We, therefore, conclude that the absorption spectral changes shown in Figure 1 can be ascribed to the equilibrium reaction

$$Ni^{II}TPP(py) + py \underset{k_b}{\overset{k_f[py]}{\rightleftharpoons}} Ni^{II}TPP(py)_2 \qquad (1)$$

Here py, $Ni^{II}TPP(py)$, and $Ni^{II}TPP(py)_2$ stand for a pyridine molecule and mono- and bis(pyridine) adducts of $Ni^{II}TPP$, respectively. On the assumption that (1) $Ni^{II}TPP(py)$ has no absorption at 599 nm and (2) the absorption spectrum at 180.3 K is solely due to $Ni^{II}TPP(py)_2$, the equilibrium constant, K, is calculated by the equation

$$K = k_f/k_b = D(D_\infty - D)^{-1}[py]^{-1}$$

where D and D_∞ are the 599-nm absorbances at T and at 180.3 K, respectively. From the plots of ln K vs. T^{-1} the enthalpy and entropy changes, ΔH and ΔS, are obtained as $\Delta H = -5.3 \pm 0.4$ kcal mol^{-1} and $\Delta S = -31.5 \pm 0.3$ cal mol^{-1} deg^{-1}.

Figure 2 shows the transient spectra observed for $Ni^{II}TPP$ in the mixed solvent of 2:3 pyridine and toluene 20 ns after the 532-nm laser pulses at 280.4 and 181.2 K. The transient spectrum measured at 280.4 K exhibits a negative peak maximum around 525 nm and positive maxima around 560 and 600 nm. The decay of the transient follows the first-order kinetics with a rate constant of $k = 9.8 \times 10^6$ s^{-1}. The transient spectrum is in good accord with the difference spectrum obtained by subtracting the spectrum of $Ni^{II}TPP(py)$ from that of $Ni^{II}TPP(py)_2$. This result implies that the photoexcited $Ni^{II}TPP(py)$ reacts with py to form $Ni^{II}TPP(py)_2$ that then releases py to regenerate $Ni^{II}TPP(py)$. At 181.2 K, the transient spectrum, which decays with the first-order rate constant of 3.3×10^4 s^{-1}, is in good agreement with the difference spectrum obtained by subtracting the spectrum of $Ni^{II}TPP(py)_2$ from that of $Ni^{II}TPP(py)$. Since the species in the solution at 180.2 K is attributed to $Ni^{II}TPP(py)_2$, photoexcited $Ni^{II}TPP(py)_2$ is concluded to release py to produce $Ni^{II}TPP(py)$, which reacts with py to regenerate $Ni^{II}TPP(py)_2$. From the flash

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(7) Kim, D.; Holten, D. *Chem. Phys. Lett.* **1983**, *98*, 584–589.
(8) Kim, D.; Kirmaier, C.; Holten, D. *Chem. Phys.* **1983**, *75*, 305–322.
(9) Yamamoto, S.; Hoshino, M.; Yasufuku, K.; Imamura, M. *Inorg. Chem.* **1984**, *23*, 195–198.

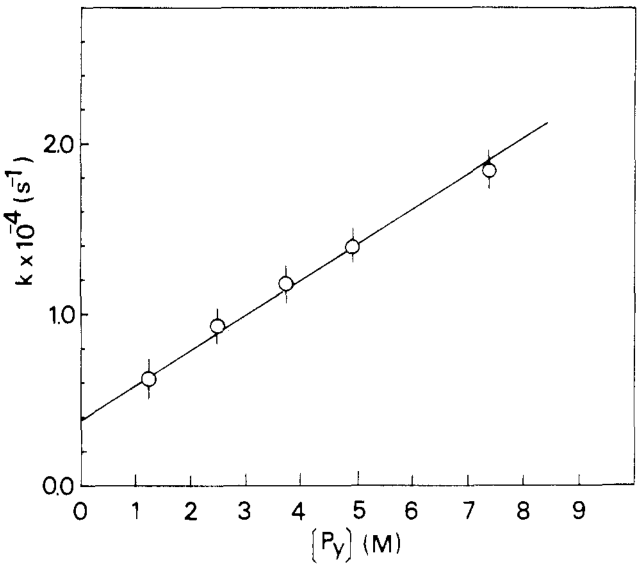

Figure 3. Plot of k vs. pyridine concentration, [py], obtained at 200 K.

photolysis studies mentioned above, the photochemical reactions of $Ni^{II}TPP$ in the mixed solvent are represented as

$$Ni^{II}TPP(py) + py \underset{\text{dark}}{\overset{h\nu}{\rightleftharpoons}} Ni^{II}TPP(py)_2 \quad (T = 280.4\text{ K}) \qquad (2)$$

$$Ni^{II}TPP(py)_2 \underset{\text{dark}}{\overset{h\nu}{\rightleftharpoons}} Ni^{II}TPP(py) + py \quad (T = 181.2\text{ K}) \qquad (3)$$

Therefore, the laser flash is considered to result in the shift of the equilibrium shown by reaction 1 owing to the photoinduced attachment of py to $Ni^{II}TPP(py)$ as well as detachment of py from $Ni^{II}TPP(py)_2$. Accordingly, the decay process of the transient is interpreted in terms of the recovery of the equilibrium: the decay rate constant, k, is expressed as

$$k = k_f[py] + k_b$$

Figure 3 shows the plot of k as a function of pyridine concentration, [py], at 200 K. From the slope and the intercept of the line, we obtain $k_f = 2.06 \times 10^4$ M^{-1} s^{-1}. The fact that k has a linear relation to [py] supports the conclusion that the photochemistry of the solution is expressed by reactions 2 and 3; i.e., the photoexcited $Ni^{II}TPP(py)_2$ releases a pyridine molecule, and the photoexcited $Ni^{II}TPP(py)$ reacts with a pyridine molecule to form $Ni^{II}TPP(py)_2$. The previous results obtained by picosecond photolysis of $Ni^{II}TPP$ in pyridine solutions were interpreted on the assumption that two pyridine molecules are concerned in the photochemistry of $Ni^{II}TPP$.[7,8] However, the present results show that only one pyridine molecule is responsible for the photochemistry of $Ni^{II}TPP$ in a mixed solvent of pyridine and toluene.

From k obtained by laser photolysis and the equilibrium constant K calculated from the spectral changes, k_f and k_b can be determined at various temperatures. The usual Arrhenius expressions for k_f and k_b are given by

$$k_f = (6.5 \pm 0.5) \times 10^7 \exp[-(3230 \pm 300)/RT]\ M^{-1}\ s^{-1}$$

$$k_b = (2.1 \pm 0.2) \times 10^{14} \exp[-(9400 \pm 500)/RT]\ s^{-1}$$

The fact that the preexponential factor in k_b exceeds 10^{13} suggests that the activation entropy for the dissociation of py from $Ni^{II}TPP(py)_2$ is necessarily a positive one.

The photochemistry of $Ni^{II}TPP(py)$ and $Ni^{II}TPP(py)_2$ is considered to be closely related to the nature of their excited states. However, neither of the excited states of $Ni^{II}TPP(py)$ and $Ni^{II}TPP(py)_2$ was observed in the present study because of their short lifetimes in comparison with the duration of the laser flash (20 ns). Straub and his co-workers[10] have carried out picosecond photolysis studies of nickel(II) protoporphyrin dimethyl ester and found two excited states having decay times of 10 and 250 ps. Picosecond photolysis studies of $Ni^{II}TPP$ in a pyridine solution at room temperature indicate that (1) the metal excited singlet state, $^1A_{1g}$, of $Ni^{II}TPP(py)_2$ releases the ligands and (2) the metal excited triplet state, $^3B_{1g}$, of $Ni^{II}TPP$ binds the ligands.[7,8] In the present study, we have reconfirmed, by using a conventional laser photolysis technique, that $Ni^{II}TPP$ in a mixed solvent of pyridine and toluene undergoes photoinduced ligand attachment and detachment. From the measurements of the decay rate constants of the transients in the temperature range 300–180 K, the apparent activation energies and entropies for k_f and k_b were determined. These results are considered to be useful for further understanding of metalloporphyrin photochemistry as well as the association and dissociation processes of ligands in metalloporphyrins.

Registry No. $Ni^{II}TPP$, 14172-92-0; $Ni^{II}TPP(py)$, 36046-97-6; $Ni^{II}TPP(py)_2$, 101056-27-3; py, 110-86-1; toluene, 108-88-3.

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(10) Straub, K. D.; Rentzepis, P. M.; Huppert, D. *J. Photochem.* **1981**, *17*, 419–425.

Contribution from the Department of Chemistry,
Faculty of Science, Shimane University, Matsue 690, Japan

Photoinduced Radical Formation of Bis(phthalocyaninato)lanthanoid(III) in a Solvent Mixture of Dichloromethane and Acetonitrile

Kuninobu Kasuga,* Hideharu Morimoto, and Motonori Ando

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A bis(phthalocyaninato)lanthanoid(III) complex, PcLnPcH (Pc = phthalocyanine dianion; Ln = lanthanoid(III) cation), has received considerable attention for its characteristic properties such as electrochromism[1] and electrical conductivity.[2] The structure of bis(phthalocyaninato)neodymium(III) was recently revealed to be of a sandwich type from an X-ray diffraction study.[3] Application of the PcLuPcH complex to an electrochromic display has also been studied by Nicholson and her co-workers.[4] The electrochromism is attributable to generation of various π-radical species that show different bright colors depending upon the applied potentials.[5]

Previously, we reported that a green radical was prepared from a blue PcNdPcH complex in a solvent mixture of dichloromethane and methanol with a chemical oxidant such as p-benzoquinone.[6] Upon photoirradiation, the radical was also generated from the blue PcLnPcH complex in the solvent mixture of dichloromethane and acetonitrile. We report here the photoinduced oxidation of the bis(phthalocyaninato)lanthanoid(III) complexes.

Experimental Section

The PcLnPcH complex, where Ln is La(III), Nd(III), Lu(III), or Y(III), was prepared and purified by the method described before.[7] The solvents used for the measurements were reagent grade and were used without further purification. The sample solution in a glass cell with a 1-cm light path length was purged by nitrogen gas and was irradiated with an Eikoshia PIH 300-W high-pressure Hg lamp through a Pyrex filter at 20 ± 2 °C (the cell was situated 3 cm away from the light

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(1) Moskalev, P. N.; Kirin, I. S. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1972**, *46*, 1019.

(2) ter Harr, L. W.; Hatfield, W. E.; Tsutsui, M. *Mol. Cryst. Liq. Cryst.* **1984**, *107*, 181.

(3) Kasuga, K.; Tsutsui, M.; Petterson, R. C.; Tatsumi, K.; Opdenbosch, N. V.; Pepe, G.; Myer, E. F., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4836.

(4) Nicholson, M.; Galiardi, R. V. *Gov. Rep. Annunce. & Index* (*U.S.*) **1977**, *77*, 112. Nicholson, M.; Weismuller, T. P. *Ibid.* **1983**, *83*, 6250 and references cited therein.

(5) Corker, G. A.; Grant, B.; Clecak, N. J. *J. Electrochem. Soc.* **1979**, *126*, 1339.

(6) Kasuga, K.; Ando, M.; Morimoto, H. *Inorg. Chim. Acta* **1986**, *112*, 99.

(7) Misumi, S.; Kasuga, K. *Nippon Kagaku Zasshi* **1971**, *92*, 335.

0020-1669/86/1325-2478$01.50/0