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The Methyl(cyclam)nickel(III) Dication in Aqueous Solutions: Determination of the Volume of Reaction and Volume of Activation for the Homolysis of the Nickel–Carbon Bond. A Pulse-Radiolysis Study

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In a recent study[2] it was reported that methyl radicals react with NiL^{2+}, where L = 1,4,8,11-tetraazacyclotetradecane (cyclam), in aqueous solutions according to the following reaction scheme:

$$NiL^{2+}(aq) + {}^{\bullet}CH_3 \overset{H_2O}{\rightleftharpoons} L(H_2O)Ni^{III}\text{–}CH_3^{2+}(aq) \tag{1}$$

$$k_1 = 6.5 \times 10^8\ M^{-1}\ s^{-1},\ k_{-1} = 57\ s^{-1},\ K_1 = 1.1 \times 10^7\ M^{-1}$$

$$L(H_2O)Ni^{III}\text{–}CH_3^{2+}(aq) + {}^{\bullet}CH_3 \rightarrow NiL^{2+}(aq) + C_2H_6 \tag{2}$$

$$2k_2 = 8 \times 10^7\ M^{-1}\ s^{-1}$$

These reactions are of special interest due to the suggestion that transients with nickel–carbon bonds, though nickel(II)–carbon compounds, are key intermediates in at least two enzymatic processes.[3]

It seemed of interest to gain more mechanistic details on the equilibrium reaction (1). Of special interest is the question whether indeed the methyl and water molecules are bound coherently or consecutively to the central nickel atom. The best approach to solve this question seemed to be the measurement of the volumes of activation of reactions 1 and −1. The results indicate that both bonds are being formed coherently.

Experimental Section

The sample preparation and the pulse-radiolysis experiments were carried out exactly as described earlier in detail.[2] The only exception to this was that a Xe–Hg arc lamp was used instead of the Xe arc lamp and all measurements were carried out at 313 nm. This change of lamps was required as the radiation intensity penetrating the high-pressure cell is small and therefore the absorption due to the transients is small. Thus, a high-intensity lamp is required in order to increase the signal to noise ratio.

The high-pressure setup was identical with that described elsewhere in detail.[4] The window of the high-pressure cell through which the radiation penetrates the cell was however replaced by a 5-mm saphire window. The internal pillbox cell was placed immediately near the window so that the high-energy electrons will have a minimal path through the surrounding water medium.

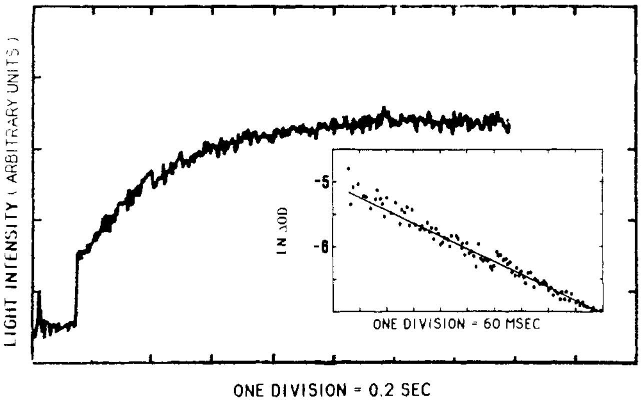

Figure 1. Computer output of the time dependence of the light transmittance of the sample following the pulse. Solution composition: 1.0 × 10^{-3} M $NiL(ClO_4)_2$, 0.1 M $(CH_3)_2SO$, 4.0 × 10^{-5} M O_2, 0.19 M N_2O (pH 3.0, pressure 150 MPa). Insert: Fit of the data to a first-order rate law.

Results and Discussion

N_2O-saturated solutions containing 1 × 10^{-3} M $NiL(ClO_4)_2$, 0.1 M $(CH_3)_2SO$, and (2.5–10) × 10^{-5} M O_2 at pH 3.0 were irradiated. Under these conditions the following reactions have to be considered.[5-8]

$$e_{aq}^- + N_2O \xrightarrow{H_3O^+} {}^{\bullet}OH + N_2 \qquad k_3 = 8.7 \times 10^9\ M^{-1}\ s^{-1}\ \text{[5]} \tag{3}$$

$$^{\bullet}OH + (CH_3)_2SO \rightarrow (CH_3)_2SOOH \qquad k_4 = 7.0 \times 10^9\ M^{-1}\ s^{-1}\ \text{[6]} \tag{4}$$

$$(CH_3)_2SOOH \rightarrow {}^{\bullet}CH_3 + CH_3SOOH \qquad k_5 = 1.5 \times 10^7\ s^{-1}\ \text{[6]} \tag{5}$$

$$NiL^{2+}(aq) + {}^{\bullet}CH_3 \overset{H_2O}{\rightleftharpoons} L(H_2O)Ni^{III}\text{–}CH_3^{2+}(aq)\ \text{[2]} \tag{1}$$

$$O_2 + {}^{\bullet}CH_3 \rightarrow {}^{\bullet}O_2CH_3 \qquad k_6 = 3.7 \times 10^9\ M^{-1}\ s^{-1}\ \text{[2]} \tag{6}$$

$$e_{aq}^- + H_3O^+ \rightarrow H + H_2O \qquad k_7 = 2.0 \times 10^{10} M^{-1}\ s^{-1}\ \text{[5]} \tag{7}$$

$$^{\bullet}OH + LNi^{2+}(aq) \rightarrow LNi^{III}(H_2O)_2^{3+} + OH^- \qquad k_8 = 2 \times 10^9\ M^{-1}\ s^{-1} \text{ at pH 3 [7]} \tag{8}$$

$$^{\bullet}CH_3 + {}^{\bullet}CH_3 \rightarrow C_2H_6 \qquad k_9 = 1.6 \times 10^9\ M^{-1}\ s^{-1}\ \text{[8]} \tag{9}$$

$$^{\bullet}O_2CH_3 + LNi^{2+}(aq) \rightarrow L(H_2O)Ni^{III}\text{–}O_2CH_3^{2+}(aq)\ \text{[2]} \tag{10}$$

Under the experimental conditions $k_3[N_2O] \gg k_7[H_3O^+]$, $k_4[(CH_3)_2SO] \gg k_8[LNi^{2+}(aq)]$ and $k_1[LNi^{2+}(aq)] \gg k_9[{}^{\bullet}CH_3]$; thus, reactions 7–9 do not contribute to the experimental observations. A comparison of $k_1[LNi^{2+}(aq)]$ with $k_6[O_2]$ indicates that under the experimental conditions a large part of the $^{\bullet}CH_3$ radicals are transformed into the transient complex $L(H_2O)Ni^{III}\text{–}CH_3^{2+}(aq)$. This then decomposes via reactions −1, 6, and 10 to form $L(H_2O)Ni^{III}\text{–}O_2CH_3^{2+}(aq)$. We followed the rate of formation of the latter complex, which has a strong absorption

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(2) Sauer, A.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1988**, *27*, 4578.

(3) (a) Sigel, H., Sigel, A., Eds. *Metal Ions in Biological Systems: Vol. 23, Nickel and Its Role in Biology*; Marcel Dekker: New York, 1988. (b) Walsh, C. T.; Oreme-Johnson, W. H. *Biochemistry* **1987**, *26*, 4901. (c) Krautler, B. *Chimia* **1987**, *41*, 277.

(4) (a) Van Eldik, R., Jonas, J., Eds. *High Pressure Chemistry and Biochemistry*; Reidel: Dordrecht, Holland, 1987. (b) Van Eldik, R., Ed. *Inorganic High Pressure Chemistry: Kinetics and Mechanisms*; Elsevier: Amsterdam, 1986.

(5) (a) Anbar, M.; Brambeneck, M.; Ross, A. B. *Natl. Stand. Ref. Data Ser.* (*U.S. Natl. Bur. Stand.*) **1973**, *NSRDS-NBS 43*. (b) Anbar, M.; Farhataziz, N.; Ross, A. B. *Ibid.* **1975**, *NSRDS-NBS 51*. (c) Farhataziz, N.; Ross, A. B. *Ibid.* **1977**, *NSRDS-NBS 59*.

(6) Veitwisch, D.; Janata, E.; Asmus, K. D. *J. Chem. Soc., Perkin Trans. 2* **1980**, 146.

(7) Zeigerson, E.; Ginzburg, G.; Meyerstein, D.; Kirschenbaum, L. J. *J. Chem. Soc., Dalton Trans.* **1980**, 1243.

(8) Hickel, B. *J. Phys. Chem.* **1975**, *79*, 1054.

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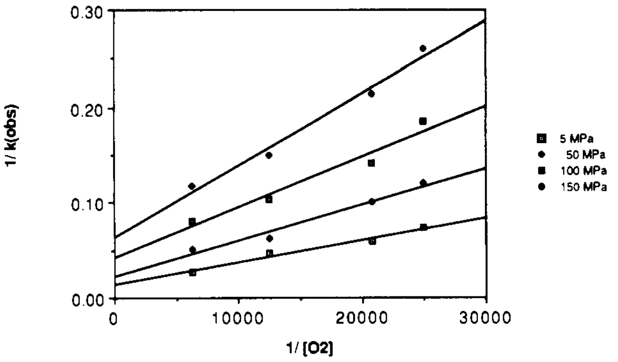

Figure 2. Dependence of the observed first-order rate constant on $1/O_2$ at different pressures. Solution composition: 1.0×10^{-3} M $NiL(ClO_4)_2$, 0.1 M $(CH_3)_2SO$, 0.11–0.19 M N_2O (pH 3.0).

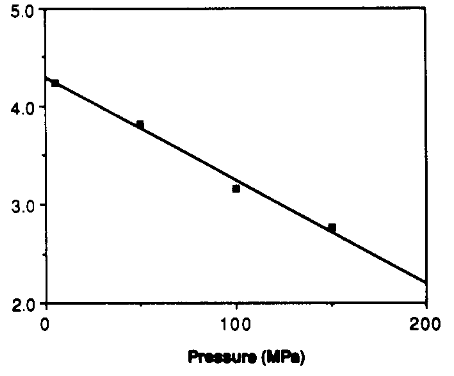

Figure 3. Dependence of ln k_{-1} on P.

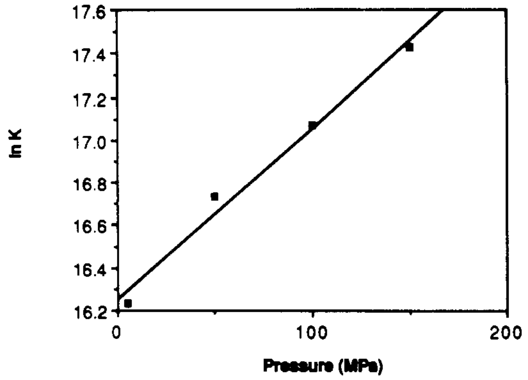

Figure 4. Dependence of ln K_1 on P.

band around 300 nm.[2] The kinetics of formation of this product obey the following rate law:

$$\frac{-\mathrm{d}[\mathrm{L(H_2O)Ni^{III}{-}CH_3}^{2+}(\mathrm{aq})]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{L(H_2O)Ni^{III}{-}O_2CH_3}^{2+}(\mathrm{aq})]}{\mathrm{d}t} = \frac{k_6k_{-1}[\mathrm{O_2}][\mathrm{L(H_2O)Ni^{III}{-}CH_3}^{2+}(\mathrm{aq})]}{k_1[\mathrm{LNi}^{2+}(\mathrm{aq})] + k_6[\mathrm{O_2}]} \quad (11)$$

i.e.

$$\frac{1}{k_{\mathrm{obs}}} = \frac{K_1[\mathrm{LNi}^{2+}(\mathrm{aq})]}{k_6[\mathrm{O_2}]} + \frac{1}{k_{-1}} \quad (12)$$

The results[2] clearly fit this mechanism. In the present study these measurements were repeated at different pressures. A typical kinetic plot is shown in Figure 1. The results are summed up in Figure 2. The figure clearly points out that the experimental findings are in accord with rate law 12 at all the pressures used. The results clearly indicate that both the value of the intercept, k_{-1}, and the slope of the plot, $K_1[\mathrm{LNi_2}^+(\mathrm{aq})]/k_6$, depend on the pressure applied.

Figure 3 shows the dependence of ln k_{-1} on P. From the slope of this plot $\Delta V^{\ddagger}_{-1} = 24.4 \pm 1.0$ cm^3 mol^{-1} is obtained. The large volume of activation is in accord with expectations for the homolysis of metal–carbon σ bonds.[9,10] This value should be compared with values reported in the literature for the homolysis of $(H_2O)_5Cr{-}R^{2+}$, which are +15.1, +26, and +20 cm^3 mol^{-1} for R = $^{\bullet}C(CH_3)_2OH$, $^{\bullet}CH(CH_3)_2$, and $^{\bullet}CH_2C_5H_4NH^+$, respectively.[9,10] It should be noted that the partial molal volumes of these R groups are considerably larger than that of the methyl group. (The molar volumes of CH_4, $CH_2(CH_3)_2$, $CH(CH_3)_2OH$, and $CH_3C_5H_4N$, estimated from density data,[11] are 28.9, 88.2, 76.5, and 97.5 cm^3 mol^{-1}, respectively, and those of the corresponding free radicals are clearly not considerably smaller.) In general there exists a good correlation between the absolute value of $\Delta V^{\ddagger}$ and the partial molar volume of the entering or leaving ligand in the case of bond formation or bond breakage, respectively.[12] Thus, from the above data we conclude that the homolysis of the nickel–carbon bond cannot account alone for the +24.4 cm^3 mol^{-1} measured. This finding is in accord with the suggestion that the homolysis of the nickel–carbon bond occurs coherently with the dissociation of the nickel–water bond trans to the nickel–carbon bond.

Figure 4 is a plot of the dependence of the ln of the slopes of the lines in Figure 2 on P. From this figure $\Delta V = -19.7$ cm^3 mol^{-1} is calculated. According to rate law 12 the slope is proportional to K_1/k_6. Therefore, the ΔV measured is expected to be a combination of the ΔV for these two steps. However, as reaction 6 is diffusion controlled, or approaches this limit, and as the viscosity of water does not change considerably in the pressure range used,[13] it is expected that $\Delta V^{\ddagger}_6$ is negligible. It is thus concluded that $\Delta\bar{V}_1 = -20 \pm 1.0$ cm^3 mol^{-1}. In light of the estimated partial molar volume of the methyl radical, see above, and the general observations that the reaction volume for addition reactions, e.g. tetrahedral to octahedral,[14] is considerably smaller than the molar volumes of the added ligands, we conclude that the absolute value of $\Delta\bar{V}_1$ is considerably larger than that expected for reaction 1a,

$$\mathrm{LNi}^{2+}(\mathrm{aq}) + {}^{\bullet}\mathrm{CH_3} \rightleftharpoons \mathrm{LNi^{III}{-}CH_3}^{2+}(\mathrm{aq}) \quad (1a)$$

in which no water–nickel bond is formed. The results thus corroborate the suggestion that a water molecule is bound as a second axial ligand to the central nickel ion. This finding is in accord with studies on other tervalent nickel complexes with tetraazamacrocyclic ligands which indicate that they are octahedral in nearly all cases studied.[15,16] It should be noted that though reaction 1 is an oxidation reaction, no large contribution from electrostriction is expected as (*a*) the charge on the complex is not changed and (*b*) though formally the nickel is oxidized from a divalent to tervalent state, the electronic distribution probably does not fully reflect this change. The nickel–carbon bond is probably better described as a somewhat polar covalent bond, as the observed homolysis process indicates, rather than an ionic bond involving a tervalent nickel ion and a carbanion.

From the values of $\Delta\bar{V}_1 = -20$ cm^3 mol^{-1} and $\Delta V^{\ddagger}_{-1} = 24.4$ cm^3 mol^{-1}, one calculates $\Delta V^{\ddagger}_1 \sim 4.0$ cm^3 mol^{-1}, i.e. the volume of activation for this reaction has a positive value, which suggests a dissociative interchange mechanism. This result seems somewhat surprising as $\mathrm{LNi}^{2+}(\mathrm{aq})$ is a planar low-spin complex and reaction 1 as written is an associative process leading to the formation of a low-spin octahedral complex.[17] The complex $\mathrm{LNi}^{2+}(\mathrm{aq})$ is

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(9) Sisley, M. J.; Rindermann, W.; van Eldik, R.; Swaddle, T. W. *J. Am. Chem. Soc.* **1984**, *106*, 7432.

(10) Ishihara, K.; Swaddle, T. W. *Can. J. Chem.* **1986**, *64*, 2168.

(11) CRC Handbook of Chemistry and Physics, 57 ed.; CRC Press: Boca Raton, FL, 1976.

(12) Van Eldik, R.; Asano, T.; Le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549.

(13) Isaacs, N. S. *Liquid Phase High Pressure Chemistry*; Wiley: Chichester, England, 1981.

(14) Kojima, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 603; **1988**, *61*, 385.

(15) Zeigerson, E.; Ginzburg, G.; Becker, J.; Kirschenbaum, L. J.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1981**, *20*, 3988.

(16) Zeigerson, E.; Bar, I.; Bernstein, J.; Kirschenbaum, L. J.; Meyerstein, D. *Inorg. Chem.* **1982**, *21*, 73.

known[19] to exist in aqueous solutions in an equilibrium with $LNi(H_2O)_2^{2+}$.

$$LNi^{2+}(aq) + 2H_2O \rightleftharpoons LNi(H_2O)_2^{2+} \qquad (13)$$

The octahedral complex $LNi(H_2O)_2^{2+}$ has the high-spin electronic configuration.[19] Pressure-dependence studies of this equilibrium reaction revealed that $\Delta\bar{V}_{13}$ is considerably smaller than expected, i.e. $\Delta\bar{V}_{13} = -1.2 \pm 0.1$ cm^3 mol^{-1} [20] or $\Delta\bar{V}_{13} = -3.5 \pm 0.1$ cm^3 mol^{-1}.[21] The authors assumed that these small volumes of reaction stem from a cancellation of a negative $\Delta\bar{V}$ coordination by a positive $\Delta\bar{V}$ expansion. The latter value stems from the change from low spin to high spin and was estimated to contribute 8.1 cm^3 mol^{-1} for the nickel–cyclam complex. This process clearly cannot contribute to $\Delta V^{\ddagger}_1$. The results thus seem to suggest that two axial water molecules, though not bound to the nickel, occupy the cavities formed by the ligand. These water molecules block the approach of the $^{\bullet}CH_3$ free radical to the central cation, and one of them has to be partially extricated from the cavity prior to the nickel–carbon bond formation. This process, which is speculative at this stage, explains the small positive value of $\Delta V^{\ddagger}_1$. We plan to extend this study to similar systems in order to check this hypothesis.

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Registry No. (cyclam)$(H_2O)Ni^{III}{-}CH_3^{2+}$, 117687-73-7.

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(17) The spin state of the complex $L(H_2O)Ni^{III}{-}CH_3^{2+}(aq)$ is not known. However, all other $L(H_2O)Ni^{III}{-}X$ or $LNi^{III}{-}X_2$ complexes, where X is a stabilizing ligand that is usually an anion, are known to have the low-spin electronic configuration.[18]

(18) (a) Zeigerson, E.; Ginzburg, G.; Schwartz, N.; Luz, Z.; Meyerstein, D. *J. Chem. Soc., Chem. Commun.* **1977**, 241. (b) Busch, D. H. *Acc. Chem. Res.* **1978**, *11*, 392. (c) Jubran, N.; Cohen, H.; Koresh, Y.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1986**, 2509.

(19) (a) Sabatini, L.; Fabbrizzi, L. *Inorg. Chem.* **1979**, *18*, 438. (b) Fabbrizzi, L. *J. Chem. Soc., Dalton Trans.* **1979**, 1857.

(20) Kitamura, Y.; Ito, T.; Kato, M. *Inorg. Chem.* **1984**, *23*, 3836.

(21) Beattie, J. K.; Kelso, M. T.; Moody, W. E.; Tregloan, P. A. *Inorg. Chem.* **1985**, *24*, 415.

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Effects of ππ Interaction on the Electronic Properties of Asymmetrical Lanthanide Porphyrin Sandwich Complexes

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Closely spaced porphyrinic macrocycles play important roles in such diverse systems as photosynthetic proteins[1] and organic conductors.[2] For example, the primary electron donor in the photosynthetic reaction center is comprised of a special pair (SP) of bacteriochlorophyll molecules.[3-5] The electronic interactions between the molecules that comprise the SP result in characteristic features such as a long-wavelength absorption in the neutral SP and a near-infrared (near-IR) absorption in the cation SP$^+$.[1c,d] One class of model systems that mimics these optical features of SP and SP$^+$ is the lanthanide and actinide porphyrin sandwich complexes [metal(porphyrin)$_2$].[6-9] In these complexes, the electronic interactions between the porphyrin π systems are extremely strong.[8,9] We have recently proposed a molecular orbital model for the sandwich dimers that accounts for the near-IR absorption band observed in the cation radicals and provides insight into the possible nature of the additional features observed in the optical spectra of the neutral compounds.[9a,b]

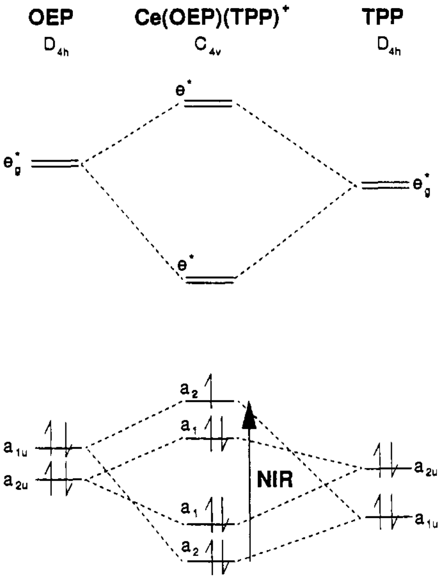

Figure 1. Partial molecular orbital diagram for Ce(OEP)(TPP)$^+$. The intradimer electronic transition that gives rise to the near-IR absorption involves promotion of an electron from an a_2 (bonding) to a_2 (antibonding) orbital and is labeled accordingly. The relative energies of the various monomer and dimer orbitals are not known; consequently, those shown in the figure were chosen for pictorial clarity only and are not to scale.

Most of the lanthanide and actinide sandwich porphyrins that have been synthesized thus far are symmetrical; that is, the two porphyrin rings are identical.[6a-f,7] In cation radicals of these complexes, the strong ππ interactions result in complete delocalization of the hole over the two porphyrin rings.[9] Recently, Holten and co-workers[8b] and Buchler and co-workers[6g,h] each reported the preparation and properties of an asymmetrical

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(1) (a) Kirmaier, C.; Holten, D. *Photosynth. Res.* **1987**, *13*, 225. (b) Budil, D.; Gast, P.; Schiffer, M.; Norris, J. R. *Annu. Rev. Phys. Chem.* **1987**, *38*, 561. (c) Hanson, L. K. *Photochem. Photobiol.* **1988**, *47*, 903. (d) Friesner, R. A.; Won, Y. *Biochim. Biophys. Acta* **1989**, *977*, 99.

(2) Hoffman, B. M.; Ibers, J. A. *Acc. Chem. Res.* **1983**, *16*, 15 and references therein.

(3) (a) Diesenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385. (b) Diesenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *Nature* **1985**, *318*, 618.

(4) Chang, C.-H.; Tiede, D.; Tang, J.; Smith, U.; Norris, J.; Schiffer, M. *FEBS Lett.* **1986**, *205*, 82.

(5) Allen, J. P.; Feher, G.; Yeates, T. O.; Rees, D. C.; Deisenhofer, J.; Huber, R. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 8589.

(6) (a) Buchler, J. W.; Kappellman, H.-G.; Knoff, M.; Lay, K.-L.; Pfeifer, S. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 1339. (b) Buchler, J. W.; Knoff, M. In *Optical Properties and Structure of Tetrapyrroles*; Blauer, G., Sund, H., Eds; de Gruyter: West Berlin, 1985; pp 91–105. (c) Buchler, J. W.; Elsasser, K.; Kihn-Botulinski, M.; Scharbert, B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 286. (d) Buchler, J. W.; De Cian, A.; Fischer, J.; Kihn-Botulinski, M.; Paulus, H.; Weiss, R. *J. Am. Chem. Soc.* **1986**, *108*, 3652. (e) Buchler, J. W.; De Cian, A.; Fischer, J.; Kihn-Botulinski, M.; Weiss, R. *Inorg. Chem.* **1988**, *27*, 339. (f) Buchler, J. W.; Scharbert, B. *J. Am. Chem. Soc.* **1988**, *110*, 4272. (g) Buchler, J. W.; Loffler, J. *Z. Naturforsch.*, in press. (h) Buchler, J. W.; De Cian, A.; Fisher, J.; Hammerschmitt, P.; Loffler, J.; Scharbert, B.; Weiss, R. *Chem. Ber.* **1989**, *122*, 2219.

(7) (a) Girolami, G.; Milam, S.; Suslick, K. *Inorg. Chem.* **1987**, *26*, 343. (b) Girolami, G.; Milam, S.; Suslick, K. *J. Am. Chem. Soc.* **1988**, *110*, 2011.

(8) (a) Yan, X.; Holten, D. *J. Phys. Chem.* **1988**, *92*, 409. (b) Bilsel, O.; Rodriguez, J.; Holten, D. *J. Phys. Chem.* **1990**, *94*, 3508. (c) Bilsel, O.; Rodriguez, J.; Holten, D.; Girolami, G. S.; Milam, S. N.; Suslick, K. S. *J. Am. Chem. Soc.* **1990**, *112*, 4075.

(9) (a) Donohoe, R. J.; Duchowski, J. K.; Bocian, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 6119. (b) Duchowski, J. K.; Bocian, D. F. *J. Am. Chem. Soc.* **1990**, *112*, 3312. (c) Perng, J.-H.; Duchowski, J. K.; Bocian, D. F. *J. Phys. Chem.*, in press.

0020-1669/90/1329-4158$02.50/0 © 1990 American Chemical Society