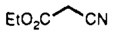
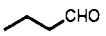
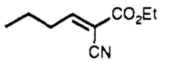
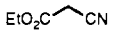
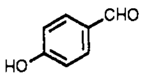
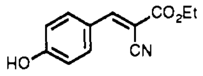
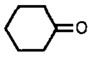
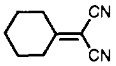
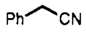
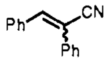
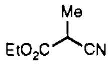
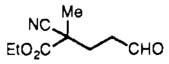
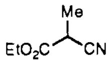
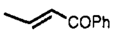
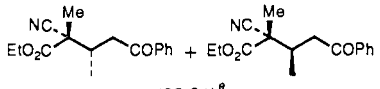
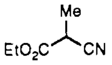
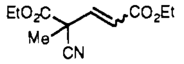
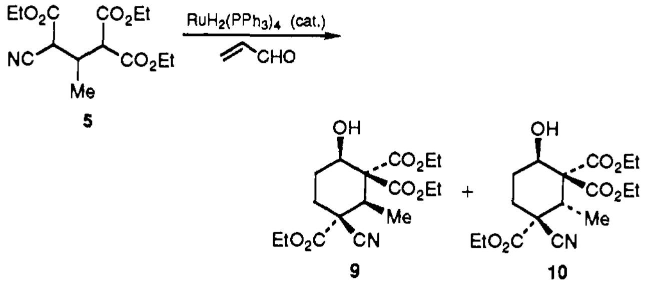
Table I. Ruthenium-Catalyzed Aldol and Michael Reaction of Nitriles[a]

entry	nitrile	electrophile	product	yield,[b] %
1			 1	83
2			 2	98
3				79
4		PhCHO	 (*E*/*Z* = 1/6)	87[c,d]
5				72
6			 (69:31)[e]	91
7		HC≡C—CO$_2$Et	 (*E*/*Z* = 65/35)	81

[a] A mixture of nitrile (2.0 mmol), carbonyl compounds or olefin (2.2 mmol), and $RuH_2(PPh_3)_4$ (0.06 mmol) in dry THF (0.5 mL) was stirred overnight at room temperature under argon. [b] Isolated yield based on the starting nitrile. [c] 1,2-Bis(diphenylphosphino)ethane (0.12 mmol) was added. [d] Reaction temperature; 60 °C. [e] Diastereomeric ratio was determined by 500 MHz ^1H NMR analysis.

contrast, the same reaction with Triton B gave **9** and **10** nonselectively (**9**/**10** = 72/28, 49% yield).



5 **9** **10**

The present ruthenium-catalyzed reactions can be rationalized by assuming a mechanism which involves an oxidative addition of a low-valent ruthenium species into the C–H bond adjacent to the cyano groups.[9] The chemoselectivity toward nitriles clearly indicates the coordination of the cyano group to the low-valent ruthenium species.[10] The key step of this reaction is quite similar to those of palladium-catalyzed transalkylation[3a] and hydrolysis reactions[3b] of tertiary amines, where low-valent palladium inserts into the C–H bond adjacent to amino groups. Ittel et al. have succeeded in the isolation of the adduct of methyl cyanoacetate and low-valent $HFe(dmpe)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$).[9] Insertion of the ruthenium complexes into carbonyl compounds or alkenes and subsequent reductive elimination of ruthenium species would give aldol or Michael adducts. The coordination of the nitrile and carbonyl groups of **5** to ruthenium seems to play an important role in the diastereoselective formation of **7** and **9**.

Finally, the present reaction provides a versatile method for the addition of nitriles to acetylenic compounds (entry 7). Generally, such additions to acetylenic compounds is difficult,[11] because polycondensation[12] and nucleophilic reactions of the acetylide anion[13] proceed under the reaction conditions.

The ruthenium-catalyzed aldol and Michael reactions of nitriles disclosed above provide a potential method for chemo- and stereoselective C–C bond formation, and the origin of the high stereoselectivity arising from the coordination of ruthenium must wait further research.

Supplementary Material Available: Spectral data (^1H NMR, IR, and ^{13}C NMR) for **7**, **8**, **9** and **10** (3 pages). Ordering information is given on any current masthead page.

---

(9) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577.

(10) Coordination of ruthenium, see: Murahashi, S.-I.; Naota, T.; Saito, E. *J. Am. Chem. Soc.* **1986**, *108*, 7846.

(11) Successful examples, see: (a) Organocuprates: Marino, J. P.; Linderman, R. J. *J. Org. Chem.* **1983**, *48*, 4621 and the references cited therein. (b) Silyl enolates-$TiCl_4$: Quendo, A.; Rousseau, G. *Tetrahedron Lett.* **1988**, *29*, 6443.

(12) Woodward, R. B.; Singh, T. *J. Am. Chem. Soc.* **1950**, *72*, 494.

(13) House, H. O.; Roelofs, W. L.; Trost, B. M. *J. Org. Chem.* **1966**, *31*, 646. Grob, C. A.; Kaiser, A. *Helv. Chim. Acta* **1967**, *50*, 1599.

The Nitrogen Atom Transfer Reactivity of Nitridomanganese(V) Porphyrins with Chromium(III) Porphyrins

Lawrence A. Bottomley* and Frank L. Neely

School of Chemistry and Biochemistry
Georgia Institute of Technology
Atlanta, Georgia 30332-0400

Received November 1, 1988

The oxygen atom transfer reactivity of inorganic molecules has been avidly investigated during the past three decades.[1] Much of this work has utilized O═M complexes (where M may possess up to four d electrons) as the oxygen atom reagent and either phosphines, olefins, or paraffins as the oxygen atom acceptor. However, when metal complexes are utilized as the oxygen atom acceptor, binuclear, μ-oxo-bridged complexes are the usual product.[2] Complete intermetal oxygen atom transfer has been

---

(1) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401-1449.

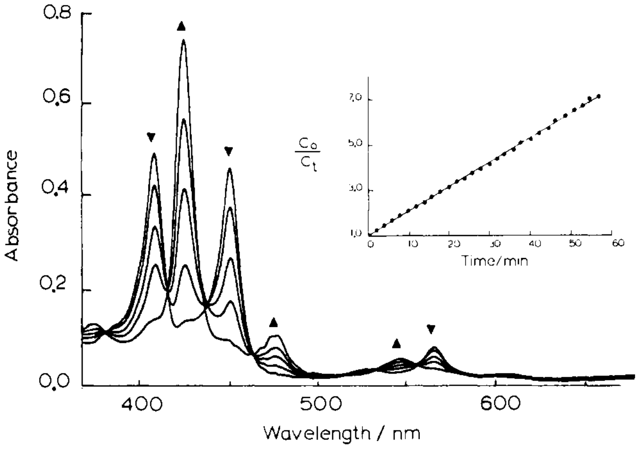


Figure 1. Electronic spectra acquired as a function of time after mixing equal volume aliquots of a 6.2 × 10^{-5} M NMn(OEP) and a 6.2 × 10^{-5} M ClCr(TPP) solution in a cuvette with an optical path length of 0.071 cm. The inset is the typical $1/C_t$ vs time plot, a diagnostic indicator of a reaction first order in each of the reactants and second order overall. The ordinate has been normalized to the initial concentration of ClCr(TPP) for the purposes of display. An identical trace was observed for the change in concentration of NMn(OEP) as a function of time.

demonstrated but only in a limited number of cases.[3]

The reactivity of oxo-metalloporphyrins has also been actively pursued since these materials serve as mimics of the active sites of heme-containing monooxygenases.[4-6] Recently, we[7,8] and others[9-11] have explored the reactivity of nitrido Mn porphyrins. Interest in these materials stems from the observation that the N≡Mn core is isoelectronic with O═Fe, the reactive moiety involved in the oxygen atom transfer reactivity in vivo. In this report, we present the first evidence of complete intermetal nitrogen atom transfer. This reaction involves a net, two-electron process through a transient μ-nitrido-bridged bimetallic intermediate.

Reaction of N≡Mn^{V}(OEP)[12] with Cl—Cr^{III}(TPP)[12] in benzene proceeds rapidly, irreversibly, and quantitatively to the products Cl—Mn(OEP) and N≡Cr(TPP) as given in eq 1. Electronic

$$\mathrm{N{\equiv}Mn(OEP) + Cl{-}Cr(TPP) \rightarrow Cl{-}Mn(OEP) + N{\equiv}Cr(TPP)} \quad (1)$$

absorption spectra acquired during the course of this reaction are depicted in Figure 1. Well-defined isosbestic points are observed at 410, 435, and 464 nm. The final spectrum is that of a mixture of N≡Cr(TPP) and Cl—Mn(OEP) in the exact concentration ratios as that of the reactants. The kinetics of this reaction were determined from the absorbance changes as a function of time and as a function of the concentrations of each of the reactants. A typical analysis of the data is depicted in the inset of Figure 1. This reaction is first-order in each of the reactants; at 25 °C, a second-order rate constant of 48 ± 5 M^{-1} s^{-1} was obtained.

In an effort to identify any long-lived intermediates, this reaction was carried out at ambient temperature in the cavity of an EPR spectrometer. During the course of the reaction, the nine-line spectrum (centered at $g = 1.9821$) characteristic[13] of ClCr(TPP) decreased in intensity with a concomitant increase in the eleven-line spectrum characteristic[14] of N≡Cr(TPP) with a $g = 1.985$. Similarly, when the reaction was carried out in an electrochemical cell, the cyclic voltammetric fingerprints[7,15-17] of the reactants were replaced by those of the products. No new or transient redox processes were observed within the accessible solvent/supporting electrolyte potential range.

We propose that this nitrogen atom transfer reaction proceeds via backside nucleophilic attack on the five-coordinate ClCr(TPP) through a binuclear μ-nitrido intermediate. Although we have not directly observed the existence of the binuclear intermediate, evidence in support of the proposal is as follows. First, when the reaction of N≡Mn(OEP) with Cl—Cr(TPP) was carried out in the presence of pyridine (in relative concentrations of 1:1:2), the rate constant for the reaction decreased by 8-fold to 6.0 ± 1.4 M^{-1} s^{-1}. At relative concentrations of pyridine greater that 1:1:10, there was no observable reaction after 10 h. We have previously shown that pyridine readily binds to the Cr(III) center[15] but does not interact with the N≡Mn core.[7] Thus, the Cr(III) center must be accessible to the lone pair of the nitrido group for the reaction to proceed. Secondly, when the Cl—Cr(2,4,6-trimethoxy-TPP) is treated with N≡Mn(OEP), no reaction is observed. Ortho substituents on the phenyl rings have been shown to inhibit formation of μ-oxo-bridged[18] and μ-nitrido-bridged[19] Fe(porphyrin) dimers and infers a binuclear intermediate for the nitrogen atom transfer reaction. Thirdly, when the chlorochromium(III) derivative of Baldwin's C_2 capped porphyrin is treated with N≡Mn(OEP), no reaction is observed after 10 h. This observation rules out ionization of the coordinate covalently bound chloride as the initial step in the reaction sequence and lends credence to the backside nucleophilic attack hypothesis.

It is interesting to note that when the porphyrin ring structure of the reactants is interchanged, i.e., N≡Mn(TPP) is reacted with Cl—Cr(OEP), the second-order rate constant decreases by approximately one order of magnitude. This decrease in rate reflects the decrease in the nucleophilic character of the nitrido donor group and the decrease in the electrophilic character of the Cr(III) acceptor induced by modification of porphyrin structure. This parallels the trend observed for the reactions of nitrido Mn porphyrins with substituted acetic anhydrides.[8] Secondly, there was no measurable back reaction, even at reflux for several hours. Clearly, the driving force for the nitrogen atom transfer reaction between N≡Mn(porphyrin) and Cr^{III}(porphyrin) is the thermodynamic stability of the nitrido Cr product. Thirdly, when N≡Mn(OEP) is treated with Cl—Mn(TPP) or when N≡Cr(OEP) is treated with Cl—Cr(TPP), intermetal nitrogen atom transfer is also observed. We are currently exploring the reactivity

---

(2) (a) Groves, J. T.; Kruper, W. J., Jr. *Isr. J. Chem.* **1985**, *25*, 148. (b) Liston, D. J.; West, B. O. *Inorg. Chem.* **1985**, *24*, 1568. (c) Liston, D. J.; Kennedy, B. J.; Murray, K. S.; West, B. O. *Inorg. Chem.* **1985**, *24*, 1561. (d) Elliott, R. L.; Nichols, P. J.; West, B. O. *Aust. J. Chem.* **1986**, *39*, 975. (e) Saxton, R. J.; Olson, L. W.; Wilson, L. J. *J. Chem. Soc., Chem. Commun.* **1982**, 984. (f) Chin, D. H.; Balch, A. L.; La Mar, G. N. *J. Am. Chem. Soc.* **1980**, *102*, 1446 and 4344. (g) Balch, A. L.; Chan, Y.-W.; Cheng, R. J.; La Mar, G. N.; Latos-Grazynski, L.; Renner, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7779.

(3) (a) Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248. (b) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chim. Acta* **1976**, *19*, L67. (c) Harlan, E. W.; Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6992.

(4) Dawson, J. H. *Science* **1988**, *240*, 433-439, and references therein.

(5) Meunier, B. *Bull. Soc. Chim. Fr.* **1986**, 578 and references therein.

(6) McMurry, T. J.; Groves, J. T. In *Cytochrome P-450*; Ortiz de Montellano, P. R.; Ed.; Plenum: New York, 1986; Chapter 1 and references therein.

(7) Bottomley, L. A.; Neely, F. L.; Gorce, J.-N. *Inorg. Chem.* **1988**, *27*, 1300-1303.

(8) Bottomley, L. A.; Neely, F. L. *J. Am. Chem. Soc.* **1988**, *110*, 6748-6752.

(9) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073.

(10) Buchler, J. W.; Dreher, C.; Lay, K.-L. *Chem. Ber.* **1984**, *117*, 2261-2274.

(11) Woo, L. K.; Goll, J. G. *J. Am. Chem. Soc.*, in press.

(12) Abbreviations used are as follows: octaethylporphinato dianion = OEP; *meso*-tetraphenylporphinato dianion = TPP; tetrakis(2,4,6-trimethoxyphenyl)porphinato dianion = 2,4,6-trimethoxy-TPP.

(13) Newton, C. M.; Davis, D. G. *J. Magn. Reson.* **1975**, *20*, 446-457.

(14) (a) Buchler, J. W.; Dreher, C.; Lay, K.-L.; Raap, A.; Gersonde, K. *Inorg. Chem.* **1983**, *22*, 879-884. (b) Groves, J. T.; Takahashi, T.; Butler, W. M. *Inorg. Chem.* **1983**, *22*, 884-887.

(15) (a) Bottomley, L. A.; Kadish, K. M. *J. Chem. Soc., Chem. Commun.* **1981**, 1212-1214. (b) Bottomley, L. A.; Kadish, K. M. *Inorg. Chem.* **1983**, *22*, 342-349.

(16) (a) Kadish, K. M.; Kelly, S. L. *Inorg. Chem.* **1979**, *18*, 2968. (b) Kelly, S. L.; Kadish, K. M. *Inorg. Chem.* **1982**, *21*, 3631.

(17) Bottomley, L. A.; Neely, F. L. *Inorg. Chem.*, submitted for publication.

(18) Morgan, B.; Dolphin, D. In *Structure and Bonding, 64*; Buchler, J. W., Ed.; Springer-Verlag: Berlin, 1987; pp 115-204.

(19) Wagner, W.-D.; Nakamoto, K. *J. Am. Chem. Soc.* **1988**, *110*, 4044-4045.

of these and other mononuclear nitrido metalloporphyrins with metallomacrocyclic substrates to evaluate the generality of this reaction.

Acknowledgment. Support of this research by DHHS through Grant No. HL-33734 is gratefully acknowledged.

Methylamine-Assisted Solubilization of Lithium and Sodium Metals in Various Amine and Ether Solvents

Margaret K. Faber, Odette Fussâ-Rydel, Joseph B. Skowyra, Lauren E. H. McMills, and James L. Dye*

Department of Chemistry, Michigan State University
East Lansing, Michigan 48824

Received March 13, 1989

We wish to report a simple new technique for dissolving lithium metal alone or lithium plus sodium (up to equimolar sodium) in several amine and ether solvents in which the metals alone are either insoluble or only slightly soluble. These methods could provide convenient and inexpensive one-electron or two-electron reducing agents in various solvents without leaving behind nonvolatile organic compounds.

In 1970, we reported the solubilization of alkali metals in tetrahydrofuran (THF) and diethyl ether (DEE) by using dicyclohexano-18-crown-6 to complex the cation.[1] This was later extended to other solvents, metals, and crown ether and cryptand complexants[2-4] and ultimately led to the synthesis of crystalline alkalide[5,6] and electride[7,8] salts. Although solutions that contain metals and cation complexants have been extensively used in organic synthesis,[9-13] the cost of the complexants and their presence at the end of the reduction can limit their usefulness. The use of $Li^+(CH_3NH_2)_4$ instead of a cation that is complexed by a crown ether or cryptand not only enhances metal solubility but also provides an easily removed complexant.

Lithium is soluble in methylamine up to 20 mol %, which represents the metallic liquid compound $Li(CH_3NH_2)_4$,[14,15] freezing at 155 K. The vapor pressure of lithium–methylamine solutions drops suddenly at the composition corresponding to this compound,[16] which provides a convenient monitor of its formation. By controlling the temperature of the solution and of an external trap for methylamine (at a suitable lower temperature), the excess methylamine can be removed by distillation, leaving behind the pure compound. The solubility of sodium in pure methylamine has not been measured, but it is very low, probably less than 10^{-3} M. Conductivity measurements[17] and optical spectra[18] indicate the formation of primarily the solvated sodium cation and the sodium anion, Na^-. The sodium anion has unusual thermodynamic stability, so that reactions such as

$$2e^-_{solv} + Na^+ \rightarrow Na^- \tag{1}$$

and

$$e^-_{solv} + Na(s) \rightarrow Na^- \tag{2}$$

are favorable.[4,19] Thus, we anticipated that solutions of lithium in methylamine, which form $Li^+(CH_3NH_2)_4$ and e^-_{solv} upon dilution, should be able to dissolve sodium metal by reaction 2.

The first indication that $Li(CH_3NH_2)_4$ can be dissolved in solvents that do not dissolve lithium alone was the observation[19-21] that lithium enhances the stability of solutions of Cs(18C6) in 2-aminopropane and that lithium metal does not precipitate until the solution is concentrated.

Solvent and metal purification and vacuum-line synthesis methods have been previously described.[6,22] Weighed amounts of lithium and sodium if desired (or a measured length of sodium in calibrated tubing) were introduced into separate arms of a glass vessel in a helium-filled glovebox. After evacuation to ca. 10^{-5} Torr, enough methylamine was condensed in the vessel to dissolve the lithium and form an unsaturated solution (about 10 mol % lithium). If a mirror of sodium in equimolar amounts to lithium was present, agitation at ca. −40 °C over a period of several hours resulted in the complete dissolution of sodium. The ^7Li NMR spectrum showed a single peak at 2.5 ± 0.2 ppm relative to $Li^+(aq)$, while the ^{23}Na spectrum consisted of peak at −60.4 ± 0.2 ppm characteristic of Na^- in solution. When no sodium was present, thin liquid films of $Li(CH_3NH_2)_4$ showed a broad plasmon type of optical absorption spectrum similar to that of concentrated metal–ammonia solutions.[23] However, when sodium and lithium were present in equimolar amounts, thin liquid films showed only the optical peak of Na^- at 660 nm.

By distilling another solvent into the vessel that contained $Li(CH_3NH_2)_4$, either alone or with sodium, it was possible to form deep blue solutions even though neither lithium nor sodium would dissolve to an appreciable extent in the solvent used. Thus, $Li(CH_3NH_2)_4$ dissolves readily in dimethylamine and in 2-aminopropane to give concentrated deep blue solutions. When sodium was also present, the latter solvent contained Na^-, which was identified by its ^{23}Na NMR peak at −61 ± 1 ppm and its optical absorption peak at 660 nm. The addition of dimethyl ether to $Li(CH_3NH_2)_4$ resulted in liquid–liquid phase separation, a blue phase, and a less dense bronze phase. The ^7Li NMR peak at +20.4 ± 0.2 ppm at −50 °C for the bronze phase was identical with that observed for pure $Li(CH_3NH_2)_4$, while the more dilute blue phase had a peak at 23.0 ± 0.2 ppm at −50 °C.

Upon adding tetrahydrofuran (THF), diethyl ether (DEE), trimethylamine (TMA), or dimethoxyethane (DME) to $Li(CH_3NH_2)_4$, dark blue solutions were initially formed which, however, over a period of minutes became either light blue (DEE, TMA, DME) or colorless (THF) as lithium metal precipitated from the solution. The precipitation of lithium rather than decomposition, at least in DEE, TMA and DME, was indicated by the stability of the light blue solutions and the fact that they became darker blue at lower temperatures. Thus, the initial

---

(1) Dye, J. L.; DeBacker, M. G.; Nicely, V. A. *J. Am. Chem. Soc.* **1970**, *92*, 5226–5228.

(2) Dye, J. L.; Lok, M. T.; Tehan, F. J.; Coolen, R. B.; Papadakis, N.; Ceraso, J. M.; DeBacker, M. G. *Ber. Bunsenges. Phys. Chem.* **1971**, *75*, 659–662.

(3) Lok, M. T.; Tehan, F. J.; Dye, J. L. *J. Phys. Chem.* **1972**, *76*, 2975–2981.

(4) Dye, J. L. In *Electrons in Fluids*; Jortner, J., Kestner, N. R., Eds.; Springer-Verlag: Berlin–Heidelberg–New York, 1973; pp 77–95.

(5) Dye, J. L.; Ceraso, J. M.; Lok, M. T.; Barnett, B. L.; Tehan, F. J. *J. Am. Chem. Soc.* **1974**, *96*, 608–609. Tehan, F. J.; Barnett, B. L.; Dye, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 7203–7208.

(6) Van Eck, B.; Le, L. D.; Issa, D.; Dye, J. L. *Inorg. Chem.* **1982**, *21*, 1966–1970.

(7) Ellaboudy, A.; Dye, J. L.; Smith, P. B. *J. Am. Chem. Soc.* **1983**, *105*, 6490–6491. Dawes, S. B.; Ward, D. L.; Huang, R. H.; Dye, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 3534–3535.

(8) Dye, J. L.; DeBacker, M. G. *Ann. Rev. Phys. Chem.* **1987**, *38*, 271–301.

(9) Mathre, D. J.; Guida, W. C. *Tetrahedron Lett.* **1980**, *21*, 4773–4776.

(10) Barrett, A. G. M.; Godfrey, C. R. A.; Hollinshead, D. M.; Prokopiou, P. A.; Barton, D. H. R.; Boar, R. B.; Joukhador, L.; McGhie, J. F.; Misra, S. C. *J. Chem. Soc., Perkin Trans. I* **1981**, 1501–1509.

(11) Ohsawa, T.; Kobayashi, T.; Mizuguchi, Y.; Saitoh, T.; Oishi, T. *Tetrahedron Lett.* **1985**, *26*, 6103–6106.

(12) Pez, G. P.; Mador, I. L.; Galle, J. E.; Crissey, R. K.; Forbes, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 4098–4100.

(13) Jedlinski, Z.; Kowalczuk, M.; Kucok, P.; Grzegorzek, M.; Ermel, J. *J. Org. Chem.* **1987**, *52*, 4601–4602. Jedlinski, Z.; Kowalczuk, M.; Misiolek, A. *J. Chem. Soc., Chem. Commun.* **1988**, 1261–1262.

(14) Stacey, A. M.; Johnson, D. C.; Sienko, M. J. *J. Chem. Phys.* **1982**, *76*, 4248–4254.

(15) Edwards, P. P.; Lusis, A. R.; Sienko, M. J. *J. Chem. Phys.* **1980**, *72*, 3103–3112.

(16) Hagedorn, R.; Lelieur, J. P. *J. Phys. Chem.* **1980**, *84*, 3652–3654.

(17) Dewald, R. R.; Browall, K. W. *J. Phys. Chem.* **1970**, *74*, 129–133.

(18) Lwenje, S. M.; Stupak, C. M.; Tuttle, T. R., Jr.; Golden, S. *Chem. Phys. Lett.* **1982**, *93*, 380–382.

(19) Dye, J. L. *Prog. Inorg. Chem.* **1984**, *32*, 327–441.

(20) Issa, D.; Dye, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 3781–3782.

(21) Issa, D.; Ellaboudy, A.; Janakiraman, R.; Dye, J. L. *J. Phys. Chem.* **1984**, *88*, 3847–3851.

(22) Dye, J. L. *J. Phys. Chem.* **1984**, *88*, 3842–3846.

(23) DaGue, M. G.; Landers, S.; Lewis, H. L.; Dye, J. L. *Chem. Phys. Lett.* **1979**, *66*, 169–172.

0002-7863/89/1511-5957$01.50/0