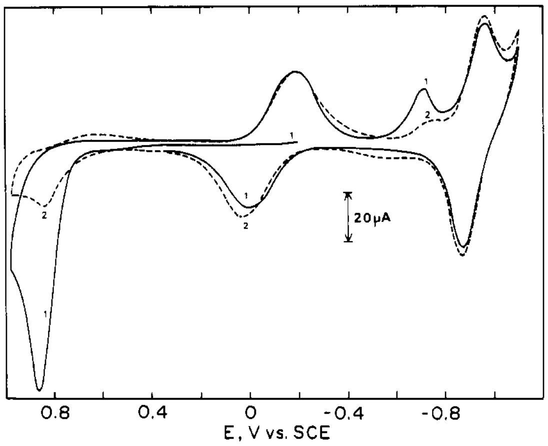

Figure 3. Cyclic voltammograms of methylcobalamin. Details are discussed in the section on electrochemical oxidation of methylcobalamin. The sweep rate was 2 mV s^{-1} at a gold minigrid, and the pH was 7.2.

observed upon reduction after a one-electron transfer produced by using γ-radiolysis methods.[10] Note that this scission must be classified as heterolytic.

Electrochemical Oxidation of Methylcobalamin. Figure 3 shows a typical thin-layer cyclic voltammogram for methylcobalamin at a gold minigrid electrode. A single irreversible wave is observed with a peak potential of +0.87 V vs. SCE on the initial positive scan. The subsequent negative scan and the second cycle (dashed line) exhibit peaks that are identical with those obtained for aquo[Co(III)]cobalamin (B_{12a}) under identical conditions. On the second cycle, the anodic peak at +0.87 V is much smaller, and on a third cycle (not shown), it cannot be observed.

Spectroelectrochemical experiments show that on oxidation of methylcobalamin at +0.80 V, B_{12a} is quantitatively produced (see labeled curve, Figure 2C). Methanol was identified by gas chromatography as the only other product. Thus, the cobalt–carbon bond is cleaved during the oxidation reaction. Controlled-potential coulometry at +0.8 V in an Au minigrid thin-layer cell gave an *n* value of 2.00 ± 0.07 for 10 determinations. It should be pointed out that neither B_{12a} nor vitamin B_{12}, cyano[Co(III)]cobalamin, show any oxidative wave before solvent breakdown in the pH range 1–11 at an Au minigrid electrode.

On the basis of these experimental results, the mechanisms for the redox reactions of the methylcobalamin and coenzyme B_{12} can be postulated. We find that the carbon–cobalt bonding and reactions can be explained with a simple two-level (σ, σ^*) molecular orbital model.[11] Oxidation at the electrode consists of a two-electron transfer out of the bonding orbital at about +0.9 V vs. SCE. The cobalt is formally Co(III). The methyl group leaves as its carbocation which, typically, will react with water as the nucleophile, producing methanol as the product.[12]

The mechanism of reduction is less obvious since only a one-electron reduction occurs. We postulate that the single electron does go into the σ^* orbital from the electrode. From electrochemical arguments at this large, negative potential, a two-electron transfer would be anticipated.[4,5] The second electron transfer is unobserved. This probably is due to the significant solvent reorganization required in analogy with the reduction of the methyl radical itself.[16] Thus, the one-electron product must be reacting relatively rapidly but away from the electrode interface to form [Co(I)]cobalamin and ethane. This formation of ethane parallels the results found when the methyl radical is formed from methylcobalamin by photolysis.[17] The reduction and concomitant heterolytic cleaving of the Co–C bond indicate that the cobalamin chelate is acting as a good leaving group. The mechanism can be explained[11,18] analogously to one-electron scission observed on reduction of alkyl halides and other organic species.[19]

Acknowledgment. The authors wish to thank Edward Deutsch for critical reading of this paper and Climaco Metral for running the GC–MS. This work was supported in part by Grant NSF-CHE 76-04321.

Registry No. Methylcobalamin, 13422-55-4; coenzyme B_{12}, 13870-90-1; aquo[Co(III)]cobalamin, 13422-52-1; [Co(I)]cobalamin, 18534-66-2; [Co(II)]cobalamin, 14463-33-3; Co, 7440-48-4.

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(10) Seki, H.; Shida, T.; Imamura, M. *Biochim. Biophys. Acta* **1974**, *372*, 100–108.

(11) Rubinson, K. A.; Parekh, H. V.; Itabashi, E.; Mark, H. B., Jr. *Inorg. Chem.*, in press.

(12) There is a possibility that the carbocation may react with one of the adjacent ring nitrogens. The properties of these have been explored in corroles and porphyrins.[13,14] The properties are similar to those of the isomers investigated by some workers.[15]

(13) Johnson, A. W.; Ward, D.; Elson, C. M. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2076–2084.

(14) Jackson, A. H. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 1, Part A, Chapter 8.

(15) Friedrich, W.; Nordmeyer, J. P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1969**, *24B*, 588–596.

(16) Toffel, P.; Henglein, A. *Faraday Discuss. Chem. Soc.* **1977**, *No. 63*, 124–133.

(17) Endicott, J. F.; Ferraudi, G. J. *J. Am. Chem. Soc.* **1977**, *99*, 243–245.

(18) Hoshino, M.; Konishi, S.; Terai, Y.; Imamura, M. *Inorg. Chem.* **1982**, *21*, 89–93.

(19) Matsui, Y.; Soga, T.; Date, Y. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 513–521. Siegel, T. M.; Mark, H. B., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 9020–9027. Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Marcel Dekker: New York, 1970; pp 201–243. Lagu, A.; Mark, H. B., Jr.; Jezorek, J. R. *J. Org. Chem.* **1977**, *42*, 1063–1067. Hill, H. A. O.; Pratt, J. M.; O'Riordan, M. P.; Williams, F. R.; Williams, R. J. P. *J. Chem. Soc. A* **1971**, 1859–1862.

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Neighboring Effects in the Ligand Field Photochemistry of the Pentacyano(ethylenediamine)ferrate(II) Complex

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Received December 14, 1981

The typical pattern observed[1,2] for the visible–near-UV photochemistry of substituted pentacyanoferrate(II) complexes, $Fe(CN)_5L^{3-}$, is the replacement of L by another ligand, as represented by reaction 1. The parallel photoreaction 2, leading to tetracyanoferrate species, has been reported to be minor or nonexistent at the irradiation wavelengths typically employed for the photolysis (e.g., 365 and 436 nm).

$$Fe(CN)_5L^{3-} + H_2O \xrightarrow{h\nu} Fe(CN)_5H_2O^{3-} + L \qquad (1)$$

$$Fe(CN)_5L^{3-} + H_2O \xrightarrow{h\nu} Fe(CN)_4(H_2O)L^{2-} + CN^- \qquad (2)$$

It has been suggested[3] that the photodissociation of a cyanide ligand would be less favored than for a neutral ligand, because of the charge separation involved in the process. Alternatively, the extent of labilization of the Fe–CN bond in the excited state would be insufficient to prevent the recombination of the quasi-dissociated species before the attack of the solvent molecules. With use of ethylenediamine as the

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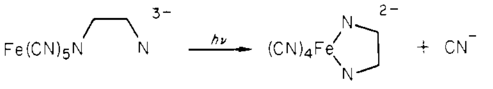
(1) J. E. Figard and J. D. Petersen, *Inorg. Chem.*, **17**, 1059 (1978).

(2) A. Vogler and H. Kunkely, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **30B**, 355 (1975).

(3) G. L. Geoffroy and M. S. Wrighton, "Organometallic Photochemistry", Academic Press, New York, 1979, p 270.

ligand L, there is a chance that the terminal NH_2 group might assist the dissociation of the cyanide ion from the metal, perhaps by forming an incipient chelate ring in the excited complex. The complete labilization of the cyanide ion would thus allow for a ring closure process, yielding a tetracyanoferrate(II) complex with a bidentate ethylenediamine ligand, as in reaction 3. To test this hypothesis, we have investigated the photochemistry of the pentacyano(ethylenediamine)ferrate(II) complex in aqueous solution.



(3)

Experimental Section

The complex $Na_3Fe(CN)_5NH_3{\cdot}3H_2O$ was prepared as described in the literature.[4] The pentacyano(ethylenediamine)ferrate(II) complex was synthesized from the previous compound in the presence of a high excess of ethylenediamine.[5] The tetracyano(ethylenediamine)ferrate(II) complex was prepared as described by Goto et al.[6] All other chemicals were reagent grade and used as supplied.

The photolysis of the $Fe(CN)_5en^{3-}$ complex was carried out with a Hanau St-75 mercury lamp, equipped with a Coleman 12225 filter, which transmits essentially the 366- and 334-nm emission lines, of relative intensities 100 and 7, respectively. All the experiments were performed at 25 °C, with use of 5 cm pathlength quartz cells under argon atmosphere, in the presence of variable amounts of ethylenediamine.

The quantum yields were based on ferrioxalate actinometry[7] and on the analysis of the cyanoiron species. The $Fe(CN)_5en^{3-}$ complex was analyzed spectrophotometrically, after a ligand-exchange reaction with pyrazinamide in large excess was carried out, for at least 40 min in the dark. The $Fe(CN)_4en^{2-}$ complex that resulted from the photolysis was isolated by ionic-exchange separation, after the excess of $Fe(CN)_5en^{3-}$ was converted to $Fe(CN)_5isonic^{4-}$ in the presence of an excess of lithium isonicotinate. This procedure was necessary in order to improve the separation with the AgI-X2 Bio-Rad (Cl^-) resin by modifying the charge of the labile species, with no effect on the nature of the photochemical product. The isolated $Fe(CN)_4en^{2-}$ complex was then detected spectrophotometrically and checked by the oxidation reaction with ferricyanide at pH 12.5, forming a deep red tetracyano diimine complex.[8]

All absorption spectra and absorbance measurements were recorded on a Cary 17 spectrophotometer. The contribution of thermal reactions (usually negligible) was controlled by the use of a dark sample that was prepared in a manner identical with that used for the photolyzed sample.

Results and Discussion

The electronic spectrum of the $Fe(CN)_5en^{3-}$ complex shows an absorption band at 395 nm ($\epsilon = 4.6 \times 10^2\ M^{-1}\ cm^{-1}$), which can be assigned to a ligand field transition from the $^1A_1$ ground state to the $^1E(1)$ component of the $^1T_{1g}$ state of O_h symmetry. The second $^1A_2$ component is expected around 325 nm by comparison with the $Fe(CN)_6^{4-}$ ion. The energy of the observed ligand field transition of $Fe(CN)_5en^{3-}$ is close to the corresponding transition in the pentacyanoferrate(II) complexes of aromatic N heterocycles.[9,10]

The excitation in the metal-to-ligand charge-transfer bands of the N-heterocyclic complexes has been reported to yield photosubstitution of these ligands with high quantum yields.[1] A similar behavior has been observed in the ligand field excitation of the $Fe(CN)_5CO^{3-}$[2,11] and $Fe(CN)_5AsO_3H_3^{3-}$[12] complexes. Analogously, the photolysis of *cis*- and *trans*-$Fe(CN)_2(CNCH_3)_4$ has been reported[13] to give only $Fe(CN)_2(CNCH_3)_3H_2O$ as the initial primary photoproduct. The nature of the photoreactive excited states has been suggested[1] as ligand field in character, namely, ^3E or $^3A_2$. It is interesting to note that CO, $CNCH_3$, and CN^- are similar in their overall ligand field strengths. The several photochemical rules[14,15] would thus predict that aquation of either ligand could occur, instead of the specific labilization of CO and $CNCH_3$.

Table I. Quantum Yields of Ligand Field (366-nm) Photolysis of Some Cyanoiron Complexes

complex	ligand released	quantum yield	remarks
$Fe(CN)_5en^{3-}$	CN^-	0.086	9% photolysis[a]
	CN^-	0.089	17% photolysis[a]
	CN^-	0.089	25% photolysis[b]
	CN^-	0.084	27% photolysis[a]
	CN^-	0.078	36% photolysis[b]
$Fe(CN)_5AsO_3H_3^{3-}$	AsO_3H_3	0.09	0 °C, pH 6–8[c]
$Fe(CN)_5CO^{3-}$	CO	0.9	*d*
	CO	0.23	0.50 M KCl[e]
$Fe(CN)_6^{4-}$	CN^-	0.1	*f*
	CN^-	0.4	*g*
$Fe(CN)_5pz^{3-}$	pz	0.15	*h*
$Fe(CN)_5Mpz^{2-}$	Mpz^+	0.010	*h*
cis-$Fe(CN)_2(CNCH_3)_4$	$CNCH_3$	0.14	*i*
trans-$Fe(CN)_2(CNCH_3)_4$	$CNCH_3$	0.13	*i*

[a] This work; $[Fe(CN)_5en^{3-}] = 1.7 \times 10^{-3}$ M, $[en] = 1.8 \times 10^{-2}$ M. [b] This work; $[Fe(CN)_5en^{3-}] = 2.0 \times 10^{-3}$ M, $[en] = 3.1 \times 10^{-2}$ M. [c] In the presence of nitrosobenzene.[12] [d] 300–370 nm.[2] [e] In the presence of imidazole.[11] [f] From pH measurements.[16] [g] In the presence of nitrosobenzene.[17] [h] In the presence of pyridine.[1] [i] 254, 280, 313 nm.[13]

On the basis of the normal photochemical behavior of the pentacyanoferrates, the photoexcitation in the $^1E(1)$ ligand field band of $Fe(CN)_5en^{3-}$ would lead essentially to the loss of ethylenediamine, as represented by eq 1. However, in the presence of an excess of ethylenediamine, this photochemical reaction is rendered ineffective by the rapid combination of the products, regenerating the starting complex.

The $Fe(CN)_4en^{2-}$ complex, in contrast with the pentacyano analogue,[5] was found to be very inert to substitution. This property eliminates the contribution of back-reaction 3, allowing one to analyze for both tetracyano and pentacyano species, independently.

The photolysis of the $Fe(CN)_5en^{3-}$ complex carried out at 366 nm, in the presence of ethylenediamine, produced only a small decay of the absorption at 395 nm. Unfortunately, the spectra of the starting complex and of the products of photolysis ($Fe(CN)_4en^{2-}$, $\lambda_{max} = 393$ and 315 nm, $\epsilon = 3.5 \times 10^2$ and $3.7 \times 10^2\ M^{-1}\ cm^{-1}$, respectively) were too similar, precluding the direct analysis of the photochemical reaction. For this reason, the $Fe(CN)_5en^{3-}$ ion was converted to the deep red pentacyano(pyrazinamide)ferrate(II) complex, while the $Fe(CN)_4en^{2-}$ complex, which does not react with pyrazinamide, was separated by ionic exchange, as described in the Experimental Section.

The quantum yields based on the decay of the $Fe(CN)_5en^{3-}$ complex agreed quantitatively with those obtained by the analysis of the $Fe(CN)_4en^{2-}$ product. Some of the typical results are shown in Table I. A systematic decrease of the

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(4) G. Brauer, "Handbook of Preparative Inorganic Chemistry", Vol. 2, 2nd ed., Academic Press, New York, 1965, p 1511.
(5) J. A. Olabe and P. J. Aymonino, *J. Inorg. Nucl. Chem.*, **36**, 1221 (1974).
(6) M. Goto, M. Takashita, and T. Sakai, *Inorg. Chem.*, **17**, 314 (1978).
(7) C. A. Parker, *Proc. R. Soc. London, Ser. A*, **220**, 104 (1953).
(8) V. Goedken, *J. Chem. Soc., Chem. Commun.*, 207 (1972).
(9) H. E. Toma, E. Giesbrecht, J. M. Malin, and E. Fluck, *Inorg. Chim. Acta*, **14**, 11 (1975).
(10) H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039 (1973).
(11) H. E. Toma, N. M. Moroi, and N. Y. Murakami Iha, *An. Acad. Bras. Cienc.*, in press.
(12) J. Legros, *J. Chem. Phys.*, **61**, 923 (1964).
(13) G. Condorelli, L. Giallongo, A. Guiffrida, and G. Romeo, *Inorg. Chim. Acta*, **7**, 7 (1973).
(14) A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).
(15) M. S. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, **5**, 165 (1973).
(16) V. Carassiti and V. Balzani, *Ann. Chim. (Rome)*, **50**, 782 (1960).
(17) G. Emschwiller and J. Legros, *C. R. Hebd. Seances Acad. Sci.*, **261**, 1535 (1965).

quantum yields was observed after 25% photolysis and was ascribed to the decay of the products in parallel with the primary process.

An interesting example has been described in the literature, illustrating the exhaustive photolysis of the ferrocyanide ion in the presence of bipyridyl or phenanthroline.[18] From this work, it became apparent that a ligand like phenanthroline could give some evidence for labile tetracyano intermediates. Due to its rigidity, 1,10-phenanthroline does not coordinate to the pentacyanoferrate(II) ion. On the other hand, the $Fe(CN)_4(H_2O)_2^{2-}$ and $Fe(CN)_4(H_2O)L^{2-}$ intermediates are expected to be labile and thus to react with 1,10-phenanthroline, forming $Fe(CN)_4phen^{2-}$.

The photolysis of the $Fe(CN)_5en^{3-}$ complex, carried out in the presence of phenanthroline, yielded $Fe(CN)_4en^{2-}$ as the major product, with an approximate quantum yield of 0.063. The $Fe(CN)_4phen^{2-}$ complex was also found, but in small amounts, with a quantum yield smaller than 0.01, along with traces of $Fe(CN)_2(phen)_2$ and $Fe(phen)_3^{2+}$ species.

Independently of the mechanism involved, one can see that the photolabilization of the cyanide ion does take place with relatively high quantum yields in the $Fe(CN)_5en^{3-}$ complex. The efficiency is comparable to the normal substitution of L in the $Fe(CN)_5L^{3-}$ complex, induced by direct ligand field excitation, as shown in Table I. On the other hand, it is certainly much higher than one would expect for reaction 2, where the regeneration of the quasi-dissociated species is likely to be more efficient than the attack of the solvent molecules. Then, it seems reasonable that, by forming an incipient chelate ring in the excited state, the ethylenediamine ligand could overcome this kind of effect in the pentacyanoferrates.[19]

An analogous behavior has also been found in the photolysis of metal hexacarbonyls,[3] where in the presence of monodentate ligands the monosubstituted species $M(CO)_5L$ are produced as the major species, while with bidentate ligands the chelate species $M(CO)_4(Chel)$ predominate.

Acknowledgment. A fellowship from CNPq (N.Y.M.I.) is gratefully acknowledged.

Registry No. $Fe(CN)_5en^{3-}$, 82482-32-4; $Fe(CN)_4en^{2-}$, 82494-75-5; $Fe(CN)_4phen^{2-}$, 17455-55-9; 1,10-phenanthroline, 66-71-7; ethylenediamine, 107-15-3.

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(18) V. Balzani, V. Carassiti, and R. Soto Loos, *Ann. Chim. (Rome)*, **54**, 103 (1964).

(19) The possibility that the photoexcited $Fe(CN)_5en^{3-}$ complex undergoes associative attack by the excess ethylenediamine is not supported by the concentration dependence experiments shown in Table I.

Communications

Direct MCD Identification of Electronic Excited States of *trans*-$Mo(CO)_4[P(n\text{-}Bu)_3]_2$ and the MO Origins and MO Fates of the Excitation Processes

Sir:

Several authors[1] recently concerned themselves with electronic excited states of substituted group 6 (Cr, Mo, W) carbonyl complexes and made direct state assignments using MCD spectroscopy. The MCD of parent molecules $M(CO)_6$ has also been reported.[2] In this publication we report the measurement and interpretation of the MCD spectrum of a trans tetracarbonyl, *trans*-$Mo(CO)_4[P(n\text{-}Bu)_3]_2$, with interesting results about the four lowest energy spin-allowed excited states. The study of this first trans carbonyl was needed because u ← g charge-transfer bands can be differentiated from all d–d bands. MCD spectra are complemented with 77 and 300 K optical data. Firm state and orbital assignments are made. The results so obtained are also interesting because band polarizations cannot come from crystal spectroscopy since there is no suitable optical host for such carbonyl molecules. Furthermore, polarized crystal spectra can almost never differentiate between the details of the MO nature for two possible excited-state assignments, $^1E_1{}^a$ and $^1E_u{}^b$. This differentiation can be made by MCD if opposite-sign *A* terms are present due to their different configurational compositions. The present findings have interesting implications in the areas of photochemistry and electronic structures of carbonyl complexes.

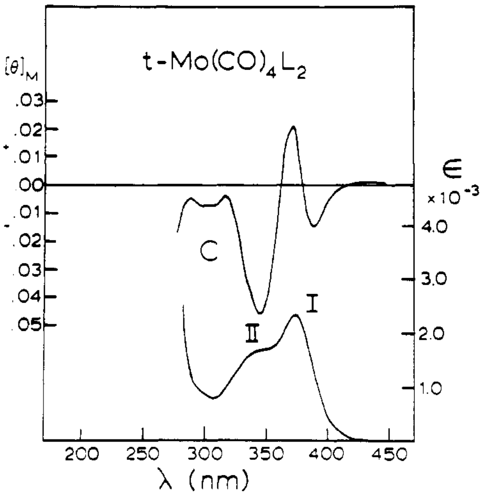

Figure 1. Room-temperature optical and MCD solution spectra of *trans*-$Mo(CO)_4[P(n\text{-}Bu)_3]_2$ in cyclohexane. $[\theta]_M$ is the molar ellipticity for a field intensity of 1 G, and ϵ has units $M^{-1}\ cm^{-1}$.

Quantities of *trans*-$Mo(CO)_4[P(n\text{-}Bu)_3]_2$ having the same properties (IR, optical, melting point) were synthesized from each of two procedures by modifying one (method A) that starts with $Mo(CO)_6$[3] and using a second one that starts with

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(1) (a) MCD data on numerous chromium, molybdenum, and tungsten pentacarbonyl amine molecules and others of A. F. Schreiner, S. Amer, and W. M. Duncan have appeared: R. M. Dahlgren, Ph.D. Dissertation, UCLA, 1978; R. M. Dahlgren and J. I. Zink, *J. Am. Chem. Soc.*, **101**, 1448 (1979); *Inorg. Chem.*, **18**, 597 (1979). (b) A. F. Schreiner, S. Amer, W. M. Duncan, R. M. Dahlgren, and J. I. Zink, Abstracts, 178th Natinal Meeting of the American Chemical Society, Washington, D.C., Sept. 1979, No. INOR 219. (c) G. Boxhoorn, D. J. Stufkens, P. J. F. M. van de Coolwijk, and A. M. F. Hezemans, *J. Chem. Soc., Chem. Commun.*, 1075 (1979). (d) A. F. Schreiner, S. Amer. W. M. Duncan, R. M. Dahlgren, and J. I. Zink, *J. Am. Chem. Soc.*, **102**, 6871 (1980). (e) A. F. Schreiner, S. Amer, W. M. Duncan, and R. M. Dahlgren, *J. Phys. Chem.*, **84**, 2688 (1980). (f) G. Boxhoorn, D. J. Stufkens, P. J. F. M. van de Coolwijk, and A. M. F. Hezemans, *Inorg. Chem.*, **20**, 2778 (1981).

(2) (a) A. F. Schreiner, R. G. Denning, P. J. Hauser, S. W. Lin, and E. H. Hopcus, "Magneto-Optical Activity of Cubic Complexes", paper presented at the Symposium on Molecular Structure and Spectroscopy, Columbus, OH, 1970; (b) A. M. F. Hezemans, J. F. M. van de Coolwijk, D. J. Stufkens, and G. Boxhoorn, *Chem. Phys. Lett.*, **73**, 550 (1980); (c) S. K. Chastain and W. R. Mason, *Inorg. Chem.*, **20**, 1395 (1981).

(3) S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Am. Chem. Soc.*, **89**, 5573 (1967).

0020-1669/82/1321-3575$01.25/0