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Mixed-Valence Properties of Ligand-Bridged Iron–Cyano Complexes

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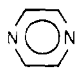
Ligand-bridged iron–cyano complexes $[(NC)_5Fe{-}L{-}Fe(CN)_5]^{4-,5-,6-}$ have been prepared with L = pyrazine, 4,4′-bipyridine, and *trans*-1,2-bis(4-pyridyl)ethylene. The mixed-valence species are generated as intermediates in the two-electron redox process $[Fe^{III}{-}L{-}Fe^{III}]^{4-} + 2e^- \rightleftarrows [Fe^{II}{-}L{-}Fe^{II}]^{6-}$. For all the bridging ligands investigated the equilibrium constant of the reaction $[Fe^{III}{-}L{-}Fe^{III}]^{4-} + [Fe^{II}{-}L{-}Fe^{II}]^{6-} \rightleftarrows 2[Fe^{II}{-}L{-}Fe^{III}]^{5-}$ is close to the value for a statistical distribution. The intervalence absorption of the mixed-valence ions is observed between 0.77 and 0.83 μm^{-1} depending only very slightly on the bridging ligand. The intensity of the intervalence band corresponds to a very small degree of electron delocalization. Vibrational frequencies deduced from the temperature dependence of the half-width of the intervalence band agree with metal to ligand stretching frequencies.

Introduction

In recent papers a wide variety of ligand-bridged ruthenium–ammine complexes exhibiting mixed-valence transitions in the near-infrared have been described.[1–5] The bridging ligand in these binuclear complexes was usually a heterocyclic nitrogen donor but various dinitriles have been studied as well. Many of the compounds $Ru^{II}{-}L{-}Ru^{III}$ are considered to belong to class II of the Robin–Day classification;[6] i.e., the oxidation states of the two metallic centers are still well defined and only a weak coupling between the coordination centers is observed. A decisive factor of the chemical properties of the mixed-valence ruthenium–ammine complexes is the pronounced tendency of the $Ru^{II}(NH_3)_5$ moiety to participate in a strong π back-bonding arrangement with suitable π acceptors such as pyrazine,[1] bipyridine,[2,3] and nitriles.[5]

A strikingly analogous behavior has been found for the $Fe^{II}(CN)_5$ unit having the same low-spin $t_{2g}{}^6$ configuration as $Ru^{II}(NH_3)_5$.[7,8] Stable complexes $Fe(CN)_5L^{3-}$ with L representing a heterocyclic nitrogen ligand have been prepared and their spectroscopic properties reported including a description of the pyrazine-bridged binuclear Fe(II) complex.[9] In analogy to the corresponding pentaammineruthenium(II) complexes the electronic spectrum of the pentacyanoiron(II) compounds with heterocyclic nitrogen ligands is dominated by a strong $t_{2g} \rightarrow \pi^*$ transition in the visible region. On the other hand the close chemical relationship between $Ru^{II}(NH_3)_5$ and $Fe^{II}(CN)_5$ has not been extensively exploited to study the mixed-valence behavior of complexes of the type $(NC)_5Fe^{II}{-}L{-}Fe^{III}(CN)_5$. Preliminary data have been reported of compounds where L is represented by cyanide[10,11] and pyrazine.[12]

We have prepared a series of complexes $[(NC)_5Fe{-}L{-}Fe(CN)_5]^{z-}$ and we have studied the spectroscopic and spectroelectrochemical properties of the various combinations of oxidation states of iron. L is pyrazine (pyz), 4,4′-bipyridine (4,4′-bpy), and *trans*-1,2-bis(4-pyridyl)ethylene (BPE). This work was undertaken in order to study the ligand-assisted electronic interaction between the two iron centers and to search for analogies to and differences in the corresponding ruthenium compounds.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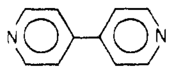
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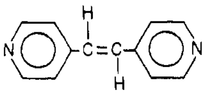
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Experimental Section

Materials. Starting reagents $Na_2[Fe(CN)_5NO]\cdot 2H_2O$, $Na_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, and the ligands were purchased in the best purity available and used without further purification. For electrochemical and spectroscopic measurements tap water was doubly distilled. Bromine water, approximately 0.02 M in 0.5 M KBr, was prepared immediately before use and standardized against $Na_2S_2O_3$.

Preparations. $Na_3Fe(CN)_5L$ (L = pyrazine (pyz), 4,4′-bipyridine (4,4′-bpy), and *trans*-1,2-bis(4-pyridyl)ethylene (BPE)) was synthesized according to published methods.[7] Shepherd's procedure[8] was used for the preparation of $Na_3Fe(CN)_5NH_3$. $Na_6[(NC)_5Fe{-}L{-}Fe(CN)_5]$ was prepared by dissolving $Na_3Fe(CN)_5NH_3$ and the appropriate amount of the bridging ligand L in water (approximately 0.2 M). This solution was kept for 15 h at room temperature. The solvent was evaporated on a Rotovap and the solid residue dried over $CaCl_2$. Identical results were obtained when equimolar solutions of $Na_3Fe(CN)_5NH_3$ and $Na_3Fe(CN)_5L$ were used. Completeness of the formation reaction and hence the purity of the binuclear products were demonstrated by Job plots, ^1H NMR spectroscopy, and cyclic voltammetry.

$Na_4[(NC)_5Fe{-}L{-}Fe(CN)_5]$ was obtained by oxidizing the corresponding binuclear ferrous complex with Br_2–water. The sodium salt of the resulting binuclear ferric complex was precipitated by adding ethanol/ether (1:1). The solid compound was filtered and thoroughly washed with ethanol. Lithium salts of the various complexes were prepared by ion exchange of the Na- or K-containing solutions on a Dowex 50 column loaded with the corresponding cation. Because of the small conproportionation constants (see next section) of the mixed-valence complexes $[(NC)_5Fe^{II}{-}L{-}Fe^{III}(CN)_5]^{5-}$ these species cannot be isolated as pure solid compounds. Solutions of the mixed-valence ions were generated either by oxidation of the binuclear Fe(II) complex with the appropriate amount of Br_2 water, by combining solutions of $Fe^{II}(CN)_5L^{3-}$ and $Fe^{III}(CN)_5NH_3{}^{2-}$ in stoichiometric ratio, or by mixing equimolar solutions of ligand-bridged ferrous and ferric complexes.

Analyses. C, H, N analyses were carried out by the microanalytical laboratory of Ciba-Geigy, Basel. Fe was determined photometrically as Fe $(phen)_3{}^{2+}$; Na and K were determined by acidimetric titration of an ion-exchanged solution and by atomic absorption spectroscopy.

Measurements. Electronic spectra of the complexes in aqueous solution in the UV-vis and near-IR were recorded with a Cary 17. Polyvinyl alcohol foils containing the Li salt of the complex were used for measuring spectra between 11 and 300 K. The foil was placed in a quartz tube, the lower end of which was in the Dewar of liquid helium. The temperature of the sample was adjusted by varying the evaporation rate of the helium. Potentiometric titrations of 0.01 M solutions of the complex in 0.1 M KCl + 0.001 M HCl were carried out with a 0.1 M Ce(IV) solution.[13] Cyclic voltammograms were scanned using approximately 10^{-3} M solutions of the complexes in 1 M $NaClO_4$ with a conventional three-electrode setup. The cell employed in the spectroelectrochemical experiments has been described earlier.[14]

Results

Visible Spectra. The visible part of the spectrum of the complexes $Fe(CN)_5L^{3-}$ (L = pyz, 4,4′-bpy, BPE) is dominated by a strong band between 2.0 and 2.5 μm^{-1} which has been assigned to a $t_{2g} \rightarrow \pi^*$ charge transfer. This band is not observed in the corresponding ferric complexes the spectra of which closely resemble that of the $Fe(CN)_6{}^{3-}$ ion. The assignment was made by considering the shift of this band observed upon protonation of the terminal nitrogen atom.[7] A

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Table I. Analytical Data

Compound	% C Calcd	% C Found	% N Calcd	% N Found	% H Calcd	% H Found	% Fe Calcd	% Fe Found	% Na Calcd	% Na Found
$Na_3[Fe(CN)_5pyz]\cdot 3H_2O$	27.8	27.9	25.2	25.9	2.6	2.3	14.4	14.3	17.7	17.3
$Na_3[Fe(CN)_5\text{-}4,4'\text{-bpy}]\cdot 2H_2O$	40.3	40.2	21.9	21.9	2.7	2.6	12.5	13.5	15.4	16.3
$Na_3[Fe(CN)_5BPE]\cdot 4H_2O$	40.1	40.1	19.3	20.9	3.6	3.1				
$Na_6[Fe_2(CN)_{10}pyz]\cdot 8H_2O$	22.9	22.2	22.9	22.7	2.7	2.7	15.2	15.8	18.8	19.3
$Na_4[Fe_2(CN)_{10}pyz]\cdot 6H_2O$	25.8	26.1	25.8	26.0	2.5	2.7	17.1	17.8		
$Na_6[Fe_2(CN)_{10}\text{-}4,4'\text{-bpy}]\cdot 4H_2O$	32.6	32.6	22.8	23.1	2.2	1.9	15.1	15.0	18.7	18.1
$Na_4[Fe_2(CN)_{10}\text{-}4,4'\text{-bpy}]\cdot 7H_2O$	32.2	31.7	22.5	22.5	3.0	3.1				
$Na_6[Fe_2(CN)_{10}BPE]\cdot 8H_2O$	31.6	31.6	20.1	20.2	3.1	3.1				

Table II. Charge-Transfer Spectra of $[(NC)_5Fe^{II}L]$ Complexes and Their $[(NH_3)_5RuL]$ Analogues

Ligand L	M = $Fe(CN)_5$ ν, μm^{-1}	M = $Fe(CN)_5$ log ϵ	Ref	M = $Ru(NH_3)_5$ ν, μm^{-1}	M = $Ru(NH_3)_5$ log ϵ	Ref
pyz	2.22	3.70	7	2.12	4.03	1
$pyzM^{II}$	1.97	4.12		1.87	4.54	1
4,4′-bpy	2.31	3.75		2.11	4.1	3
$4,4'\text{-bpy}M^{II}$	2.21	4.11		1.92	4.5	2
BPE	2.16	3.88		1.97	4.09	2
$(BPE)M^{II}$	2.12	4.15		1.87	4.54	2

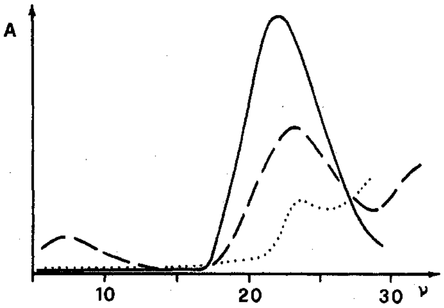


Figure 1. Absorption spectra of $[(NC)_5Fe\text{–}bpy\text{–}Fe(CN)_5]^{z-}$ at various potentials (ν in $cm^{-1} \times 10^3$): —, $z = 6$, −300 mV; - - -, $z = 5$, +150 mV; ···, $z = 4$, +700 mV. (All potentials vs. saturated sodium chloride calomel electrode.)

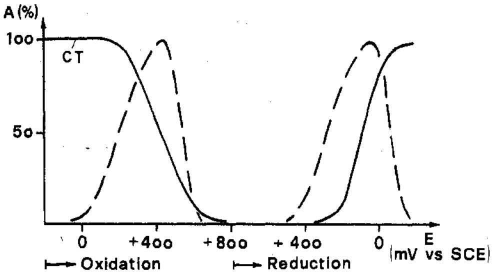


Figure 2. Spectroelectrochemistry of $[(NC)_5Fe\text{–}bpy\text{–}Fe(CN)_5]^{z-}$. Intensity of the Fe→bpy charge transfer and of the intervalence band as a function of the potential.

Table III. Mixed-Valence Data of $[(NC)_5Fe\text{-}L\text{-}Fe(CN)_5]^{5-}$ [a]

	pyz	4,4′-bpy	BPE
ν	0.83	0.83	0.77
ϵ	2200	1100	600
α^2	0.01	0.002	0.0008
$\Delta_{1/2}$(exptl)	0.48	0.50	0.48
$\Delta_{1/2}$(calcd)	0.44	0.44	0.42

[a] ν is the position of the intervalence band in μm^{-1}, ϵ is the extinction coefficient corrected for the conproportionation constant, α^2 is the delocalization parameter, and $\Delta_{1/2}$(exptl) and $\Delta_{1/2}$(calcd) are the experimental and calculated half-widths in μm^{-1}.

similar shift of the charge-transfer band is observed when another $Fe(CN)_5$ group is attached to the terminal nitrogen atom of the heterocyclic ligand. At the same time the intensity of this band is approximately doubled when going from the mononuclear to the corresponding binuclear complex. The similarity with the analogous pentaammineruthenium(II) complexes has been clearly demonstrated by the correlation of the charge-transfer energies, the correlation diagram showing a straight line with slope = 1.[7-9] Band positions and extinction coefficients of the metal to ligand charge-transfer bands of the binuclear and constituent mononuclear complexes are summarized in Table II.

Whereas the formation of binuclear ruthenium complexes can occur only with the bifunctional heterocyclic molecule as the bridging ligand, the situation of the iron–cyano compounds is more complex. In the latter case the cyanide ligand itself is ambidentate and can thus compete with the heterocycle to act as a bridge. The intensity gain of the charge-transfer band upon formation of the binuclear species, however, shows clearly the complex to be Fe–L–Fe rather than Fe–CN–Fe. No such intensity gain is observed when the binuclear complex is forced to use a cyanide ion as bridge. In this case the heterocyclic nitrogen donor is represented by pyridine, methylpyrazine, or *N*-methylpyrazinium.

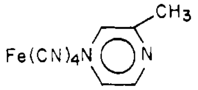
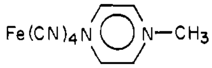
Conproportionation Constants. The equilibrium constant of the reaction involving all three combinations of oxidation states of a binuclear complex [2,2] + [3,3] ⇄ 2[2,3] covers a wide range of values. For the ruthenium complexes $[Ru^{II}\text{–}L\text{–}Ru^{III}]$ the conproportionation constant is 10^6 for L = pyz[1] whereas it is only about 4 for L = 4,4′-bpy[3] corresponding to a statistical distribution of the three species. The results of potentiometric titrations and cyclic voltammetry have been used to estimate the constants of the conproportionation equilibrium for the complexes $[(NC)_5Fe\text{–}L\text{–}Fe(CN)_5]^{4-,5-,6-}$. Only the case with L = pyz shows two waves in the cyclic voltammogram, the separation between the two peaks being about 100 mV. No well-defined peak separation could be observed for bpy and BPE as bridging ligand. The data are thus consistent with the following approximate values for the constant of the conproportionation equilibrium: 50 for L = pyz, 4 for L = 4,4′-bpy, and 4 for L = BPE. These figures clearly demonstrate that the equilibrium constants correspond very closely to a statistical situation. It is therefore hardly possible to isolate a pure salt of these mixed-valence iron species from an aqueous solution.

Near-Infrared Spectra. The ligand-bridged mixed-valence iron–cyano complexes show a broad, nearly symmetrical absorption band around 0.8 μm^{-1} which is assigned to the intervalence transfer

$$[Fe^{II}\text{-}L\text{-}Fe^{III}] \rightleftarrows [Fe^{III}\text{-}L\text{-}Fe^{II}]^*$$

This band completely vanishes upon a one-electron oxidation or reduction of the mixed-valence ions. Figure 1 shows the absorption spectra of the 4,4′-bipyridine bridged complex in its fully reduced, fully oxidized, and intermediate mixed-valence state as recorded in a spectroelectrochemical experiment. Also shown (Figure 2) are the intensities of the $t_{2g} \rightarrow \pi^*$ charge-transfer band and of the intervalence band as a function of the potential of the working electrode. The two-electron process for the overall redox reaction [3,3] + $2e^-$ ⇄ [2,2] is verified by coulometric evaluation of the cyclic voltammograms of the various binuclear complexes. Values between 1.84 and 2.13 electrons are obtained from the in-

Table IV. Intervalence Transition of ν_{IT} of Cyano-Bridged Binuclear Iron Complexes $[(NC)_5Fe\text{-}CN\text{-}Y]^{n-}$

Y	n	ν_{IT}, μm^{-1}
$Fe(CN)_5$	6	0.77
$Fe(CN)_4NH_3$	5	0.77
	5	0.77
$Fe(CN)_4NO$	4	0.72
$Fe(CN)_3$phen	4	0.73
	4	0.9

tegration of the cathodic sweep.

Discussion

The data summarized in Table III show the surprising result that the energy of the intervalence band does not depend greatly on the bridging ligand. Moreover the absorption maxima of these complexes are very close to that of the cyano-bridged mixed-valence complexes[11] (Table IV). Substitution equilibria preceding or following the intervalence transfer such as

$$[(NC)_5Fe\text{-}L\text{-}Fe(CN)_5]^{z-} \rightleftarrows [(NC)_5Fe\text{-}NC\text{-}Fe(CN)_4L]^{z-} \qquad (A)$$

have to be taken into consideration as a possible explanation for the small ligand dependence of the intervalence absorption. It has been shown, however, that bridge cleavage of analogous complexes proceeds at a very slow rate.[15] Furthermore regeneration of the [2,2] species leads to the original intensity of the charge-transfer band (Table II, Figure 2) whereas reaction A should produce spectra showing only approximately half of the intensity of this band. We thus conclude that bridge isomerism (A) occurs only to an insignificant amount.

Owing to the high negative charge of the complexes it was very difficult to study the solvent dependence of the charge-transfer and the intervalence band. Only the tetrabutylammonium salt of the pyrazine-bridged complex could be dissolved in a few nonaqueous solvents like methanol, ethanol, and dimethylformamide. The band maxima for both transitions were shifted indeed from one solvent to the other. This shift, however, did not show systematic dependence on the solvent parameters. We assume that ion-pairing effects obscure the solvent dependence of the absorption bands.

The mixed-valence iron–cyano complexes represent examples exhibiting weak coupling, i.e., belonging to class II of the Robin–Day classification.[6] The delocalization parameter α^2 obtained from the intensity of the intervalence band[16] is in the order of 0.01 or less corresponding to an electron delocalization of only 1%.

The theory of Hush[16] postulates a simple relationship between the energy of the intervalence transfer and the half-width of the absorption band of the form

$$\Delta_{1/2} = 48.06(\nu^{1/2}) \qquad (\text{cm}^{-1}, \text{at } 300 \text{ K})$$

where $\Delta_{1/2}$ is the half-width and ν the wavenumber of the absorption maximum of the intervalence band. The data in Table III are in quite good agreement with this prediction. A further test whether the mixed-valence iron–cyano complexes can be adequately described in terms of Hush's theory can be made by investigating the temperature dependence of the half-width of the intervalence band

$$\Delta_{1/2}(T) = [\Delta_{1/2}(0)]\left(\coth \frac{h\nu}{2kT}\right)^{1/2}$$

$\Delta_{1/2}(0)$ is the half-width extrapolated to $T = 0$ K and $h\nu$ the vibrational frequency participating in the Franck–Condon process of the intervalence transfer.[16] The data collected between 11 and 300 K for Fe–pyz–Fe and between 32 and 297 K for Fe–4,4′-bpy–Fe lead to vibrational frequencies of 490 cm^{-1} (pyz) and 540 cm^{-1} (4,4′-bpy). It is assumed that the metal to ligand stretching frequency is the most important vibrational mode for the intervalence transfer. This vibration is reported to be 410 (A_{1g}) and 585 (T_{1u}) cm^{-1} for $Fe(CN)_6^{4-}$ and 390 and 511 cm^{-1} for $Fe(CN)_6^{3-}$, respectively.[17] Clearly the values of $h\nu$ extracted from the temperature dependence of the intervalence absorption (Figure 3) cannot be regarded as highly accurate figures. Rather they reflect the order of magnitude and agree thus quite well with reported values of ν(M–CN). We conclude therefore that the ligand-bridged mixed-valence iron–cyano complexes represent typical examples for the weakly coupled case of mixed-valence compounds in complete analogy to the bipyridine-bridged ruthenium complex.[3] On the other hand, the pyrazine-bridged ruthenium compound[1] appears to be unique as far as its conproportionation constant and the shape of its mixed-valence band are concerned.

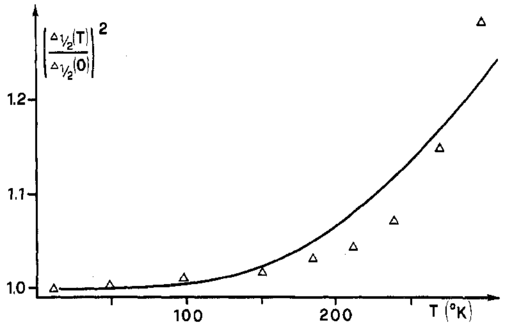


Figure 3. Temperature dependence of the half-width of the intervalence band of $[(NC)_5Fe\text{–}pyz\text{–}Fe(CN)_5]^{5-}$ (solid line, theoretical curve for $h\nu$ = 490 cm^{-1} (cf. text); Δ, experimental points).

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Registry No. $Na_3[Fe(CN)_5pyz]$, 37475-70-0; $Na_3[Fe(CN)_5\text{-}4,4'\text{-}bpy]$, 66269-64-5; $Na_3[Fe(CN)_5BPE]$, 66269-63-4; $Na_6[Fe_2(CN)_{10}pyz]$, 66269-62-3; $Na_4[Fe(CN)_{10}pyz]$, 66269-61-2; $Na_6[Fe_2(CN)_{10}\text{-}4,4'\text{-}bpy]$, 66269-60-1; $Na_4[Fe_2(CN)_{10}\text{-}4,4'\text{-}bpy]$, 66303-82-0; $Na_6[Fe_2(CN)_{10}BPE]$, 66269-59-8; $[(NC)_5Fe\text{-}pyz\text{-}Fe(CN)_5]^{5-}$, 51321-23-4; $[(NC)_5Fe\text{-}4,4'\text{-}bpy\text{-}Fe(CN)_5]^{5-}$, 66402-51-5; $[(NC)_5Fe\text{-}BPE\text{-}Fe(CN)_5]^{5-}$, 66402-52-6; $[(NC)_5Fe\text{-}CN\text{-}Fe(CN)_5]^{6-}$, 52276-15-0; $[(NC)_5Fe\text{-}CN\text{-}Fe(CN)_4NH_3]^{5-}$, 66402-53-7; $[(NC)_5Fe\text{-}CN\text{-}Fe(CN)_4(Me\text{-}pyz)]^{5-}$, 66402-54-8; $[(NC)_5Fe\text{-}CN\text{-}Fe(CN)_4NO]^{4-}$, 66402-55-9; $[(NC)_5Fe\text{-}CN\text{-}Fe(CN)_3phen]^{4-}$, 66402-56-0; $[(NC)_5Fe\text{-}CN\text{-}Fe(CN)_4(N\text{-}Me\text{-}pyz)]^{4-}$, 66402-57-1.

References and Notes

(1) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **95**, 1086 (1973).
(2) D. K. Lavallee and E. B. Fleischer, *J. Am. Chem. Soc.*, **94**, 2583 (1972).
(3) G. M. Tom, C. Creutz, and H. Taube, *J. Am. Chem. Soc.*, **96**, 7827 (1974).
(4) R. W. Callahan, G. M. Brown, and T. J. Meyer, *Inorg. Chem.*, **14**, 1443 (1975).
(5) H. Krentzien and H. Taube, *J. Am. Chem. Soc.*, **98**, 6379 (1976).
(6) M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, **10**, 247 (1967).
(7) H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039 (1973).
(8) R. E. Shepherd, *J. Am. Chem. Soc.*, **98**, 3329 (1976).
(9) J. M. Malin, C. F. Schmidt, and H. E. Toma, *Inorg. Chem.*, **14**, 2924 (1975).
(10) C. K. Jørgensen and G. Emschwiller, *Chem. Phys. Lett.*, **5**, 561 (1970).
(11) R. Glauser, U. Hauser, F. Herren, A. Ludi, P. Roder, E. Schmidt, H. Siegenthaler, and F. Wenk, *J. Am. Chem. Soc.*, **95**, 8457 (1973).
(12) F. Felix, U. Hauser, H. Siegenthaler, F. Wenk, and A. Ludi, *Inorg. Chim. Acta*, **15**, L7 (1975).
(13) C. Creutz, Ph.D. Thesis, Stanford University, 1970.
(14) K. Rieder, U. Hauser, H. Siegenthaler, E. Schmidt, and A. Ludi, *Inorg. Chem.*, **14**, 1902 (1975).
(15) A. D. James and R. S. Murray, *J. Chem. Soc., Dalton Trans.*, 1182 (1976).
(16) N. S. Hush, *Prog. Inorg. Chem.*, **8**, 391 (1967).
(17) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley-Interscience, New York, N.Y., 1970, p 183.