S(39). In the case of the Cys-Thr-Val-Cys sequence, the NH- - -S bondings in Cys(9)–NH- - -S(6) and Val(8)–NH- - -S(6) are protected by the hydrophobic side chains such as phenyl groups of Tyr and Phe residues which do not belong to the Cys(6)-X-Y-Cys(9) part.

In the Fe(II)/Z-Cys-Thr-Val-Cys-OMe complex, the NH- - -S bonds are protected by the alkyl side chain of the Val residue only. Our results indicate that reversibility of the redox couple for the Fe(II) complex of Z-Cys-Pro-Leu-Cys-OMe is primarily due to the Cys–NH- - -S and Leu–NH- - -S hydrogen bonds surrounded by the side chains of the Pro and Leu residues. On the other hand, NH- - -S hydrogen bonds in the Fe(II)/Z-Cys-Thr-Val-Cys-OMe complex are exposed to solvents without being shielded by hydrophobic groups. The side chain of the Val residue is not enough to protect the NH- - -S hydrogen bond as illustrated in Figure 6b.

Acknowledgment. We thank Professor Akitsugu Nakahara and Drs. Shin-ichiro Suzuki and Takeshi Sakurai for measurements of near-IR absorption spectra.

Registry No. $[Et_4N]_2[Fe(S_2\text{-}o\text{-xyl})_2]$, 61896-93-3.

Contribution from the Department of Chemistry, Karl-Marx-University, 7010 Leipzig, G.D.R., and Central Institute of Nuclear Research Rossendorf, 8051 Dresden, G.D.R.

The Pentachlorooxotechnetate(VI) Anion, $[TcOCl_5]^-$: An EPR Study

R. KIRMSE,*[†] J. STACH,[†] and U. ABRAM[‡]

Received May 8, 1984

The anion pentachlorooxotechnetate(VI), $TcOCl_5^-$, has been prepared by reduction of TcO_4^- with HCl in concentrated H_2SO_4 and investigated by means of the EPR technique. The axial symmetric spectrum suggests an "in-plane π-type" ground state of the MO of the unpaired electron. The $Tc–Cl_{eq}$ bonding properties have been discussed in terms of MO theory, and a comparison has been given to the bonding properties in likely complexes of neighboring elements of Tc.

Although coordination compounds of technetium have attracted a growing interest in view of their relevance in the field of nuclear medicine,[1-3] their chemistry is much less known than that of their corresponding neighboring elements. This holds true especially for compounds in which Tc possesses the formal oxidation state "+6". To our knowledge there are only very few well-characterized compounds, namely TcF_6,[4] $TcOF_4$,[5] $(NO)_2TcF_8$,[6] $TcOCl_4$,[7] $[(CH_3)_4N]_2TcO_4$,[8-10] and the trigonal-prismatic coordinated complexes tris(toluenedithiolato)technetium(VI), $Tc(tdt)_3$,[11] and tris(*o*-aminobenzenethiolato)technetium(VI), $Tc(abt)_3$.[12]

Up to now, only two EPR studies on Tc(VI) compounds have been reported, made on the trigonal-prismatic complexes $Tc(tdt)_3$[11] and $Tc(abt)_3$.[12] In the former case only the liquid-solution EPR spectrum was reported; for $Tc(abt)_3$ studies in frozen solution have been made. Therefore, the EPR behavior of Tc(VI) compounds–excluding the studies on the trigonal-prismatic ones for which, according to the symmetry, only very small ^{99}Tc hfs (hfs = hyperfine splitting) is observed—is unknown up to now. However, considering the radioactivity of technetium, EPR appears to be a very suitable method for investigating paramagnetic Tc complexes because only very small amounts of the compounds are needed.

The reduction of pertechnetate with HCl has been studied by several authors.[13-19] The formation of Tc(VI) species earlier proposed for this reaction[13] was disputed later when $[TcOCl_4]^-$ and $[TcOCl_5]^{2-}$ containing the metal in the oxidation state "+5" were isolated. In this paper we report an EPR spectroscopic investigation of the reaction of $KTcO_4$ dissolved in concentrated H_2SO_4 with a concentrated aqueous solution of HCl. After mixing of the reactants, immediately a deep blue solution was obtained, giving very intense EPR spectra that can be attributed unambiguously to a Tc(VI) complex species, most likely to $[TcOCl_5]^-$. The formation of $TcOCl_4$ cannot be excluded completely but appears not to be favored because of the conditions applied for the reduction of TcO_4^-.

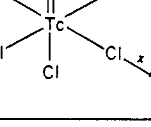

Table I. EPR Parameters for $[TcOCl_5]^-$ (Hyperfine Coupling Constants Given in 10^{-4} cm^{-1})

$\tilde{g}$	$\tilde{A}^{Tc}$
$g_\parallel = 2.057 \pm 0.003$	$A_\parallel = 230.1 \pm 2.0$
$g_\perp = 1.938 \pm 0.005$	$A_\perp = 95.8 \pm 5.0$
$\langle g_{av} \rangle^a = 1.978$	$\langle A_{av} \rangle^a = 140.6$

[a] $\langle g_{av} \rangle = (g_\parallel + 2g_\perp)/3$; $\langle A_{av} \rangle = (A_\parallel + 2A_\perp)/3$.

Lower oxidation states can be ruled out. Except for Tc compounds in the formal oxidation state "+2",[20-24] no resolved EPR signals

---

[†] Karl-Marx-University.

[‡] Central Institute of Nuclear Research Rossendorf.

(1) Jones, A. G.; Davison, A. *Int. J. Appl. Radiat. Isot.* **1982**, *33*, 867. Davison, A.; Jones, A. G. *Int. J. Appl. Radiat. Isot.* **1982**, *33*, 881.
(2) Schwochau, K. *Radiochim. Acta* **1983**, *32*, 139. Münze, R. *Isotopenpraxis* **1983**, *19*, 401.
(3) Subramanian, S. G.; Rhodes, B. A.; Cooper, J. F.; Sodd, V. J. "Radiopharmaceuticals"; The Society of Nuclear Medicine: New York, 1975.
(4) Selig, H.; Chernick, C. L.; Malm, J. G. *J. Inorg. Nucl. Chem.* **1961**, *19*, 377.
(5) Edwards, A. J.; Hugill, D.; Peacock, R. D. *Nature (London)* **1963**, *200*, 672.
(6) Holloway, J. A.; Selig, H. *J. Inorg. Nucle. Chem.* **1968**, *30*, 473.
(7) Guest, A.; Lock, C. J. L. *Can. J. Chem.* **1972**, *50*, 1807.
(8) Schwochau, K.; Astheimer, L.; Hauck, J.; Schenk, H.-J. *Angew. Chem.* **1974**, *63*, 1988.
(9) Astheimer, L.; Hauck, J.; Schenk, H.-J.; Schwochau, K. *J. Chem. Phys.* **1975**, *63*, 350.
(10) Astheimer, L.; Schwochau, K. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1131.
(11) Kakashima, M.; Koyama, M.; Fujinaga, T. *J. Inorg. Nucl. Chem.* **1976**, *38*, 801.
(12) Kirmse, R.; Stach, J.; Spies, H. *Inorg. Chim. Acta* **1980**, *45*, L 251.
(13) Ryabchikov, D. I.; Podzuyakov, A. A. *Dokl. Akad. Nauk SSSR* **1964**, *155*, 153.
(14) Münze, R.; Noll, B. *Isotopenpraxis* **1975**, *11*, 190.
(15) Spitsyn, V. I.; Glinkina, M. I.; Kusina, A. P. *Dokl. Akad. Nauk SSSR* **1971**, *200*, 1372.
(16) Dalziel, J.; Gill, N. S.; Nyholm, R. S.; Peacock, R. D. *J. Chem. Soc.* **1958**, 4012.
(17) Cotton, F. A.; Davison, A.; Day, V. W.; Gage, L. D.; Trop, H. S. *Inorg. Chem.* **1979**, *18*, 3024.
(18) Jezowska-Trzebiatowska, B.; Baluka, M. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **1965**, *13*, 1.
(19) Baluka, M.; Hanuza, J.; Jezowska-Trzebiatowska, B. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **1972**, *20*, 271.
(20) Orvig, C.; Davison, A.; Jones, A. G. *J. Labelled Compd. Radiopharm.* **1981**, *18*, 148.
(21) Heitzmann, M. W.; Yang, G. C.; Ford, L. A.; Benson, W. R. *Inorg. Chem.* **1982**, *21*, 3242.
(22) Yang, G. C.; Heitzmann, M. W.; Ford, L. A.; Benson, W. R. *J. Labelled Compd. Radiopharm.* **1981**, *18*, 535.
(23) Kirmse, R.; Lorenz, B.; Schmidt, K. *Polyhedron* **1983**, *2*, 935.

0020-1669/85/1324-2196$01.50/0

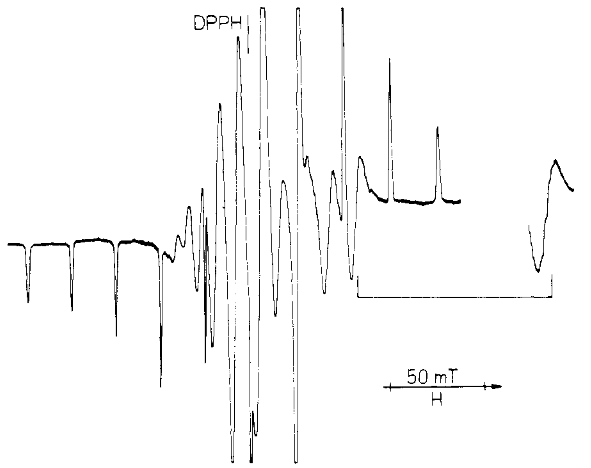

Figure 1. X-Band EPR spectrum of $[TcOCl_5]^-$ at $T = 130$ K.

are expected for the other oxidation states—Tc^{3+}, Tc^{4+}, Tc^{5+}—because of the experimental conditions applied: $T \gg 77$ K. Well-resolved EPR spectra for Tc^{3+} Tc^{4+}, and Tc^{5+} should be observed at very low temperatures, only considering the short electron spin-lattice relaxation times expected for the corresponding spin states.[25-27]

Experimental Section

Reduction of $KTcO_4$. A 1-mg sample $KTcO_4$ was added to 1 mL of concentrated H_2SO_4. To this mixture was added a drop of a concentrated aqueous solution of HCl. Immediately a deep blue solution was obtained, which was used for the EPR experiments. Attempts made to extract the blue product with $CHCl_3$ were without success.

EPR Measurements. EPR spectra were recorded in the X-band on an E-112 spectrometer (Varian) in the temperature range $130 \leq T \leq 295$ K.

Results and Discussion

Room-temperature EPR spectra of good quality could not be obtained. However, the EPR spectrum recorded at $T = 130$ K (Figure 1) is very intense and is characterized by surprisingly small EPR lines. The general features of the spectrum are characteristic for an axially symmetric, randomly oriented $S = {}^1/_2$ system with parallel and perpendicular sets of ^{99}Tc hyperfine lines (^{99}Tc, nuclear spin $I = {}^9/_2$), as described by the spin Hamiltonian

$$\hat{H}_{sp} = \beta_e[g_\parallel H_z\hat{S}_z + g_\perp(H_x\hat{S}_x + H_y\hat{S}_y)] + A_\parallel{}^{Tc}\hat{S}_z\hat{I}_z + A_\perp{}^{Tc}(\hat{S}_x\hat{I}_x + \hat{S}_y\hat{I}_y) + Q'[\hat{I}_z{}^2 - {}^1\!/_3 I(I + 1)] \quad (1)$$

where $g_\parallel$, $g_\perp$, $A_\parallel{}^{Tc}$, and $A_\perp{}^{Tc}$ are the principal values of the $\tilde{g}$ and the ^{99}Tc hyperfine interaction tensor $\tilde{A}^{Tc}$ and Q' is the ^{99}Tc quadrupole coupling constant. These parameters were obtained by use of the usual second-order expressions;[28] Q' is small and was neglected. The measured spin Hamiltonian parameters are listed in Table I.

In the perpendicular part of the spectrum an additional splitting of 9×10^{-4} cm^{-1} was observed due to the interaction of the unpaired electron with the equatorial (x, y) chlorine ligands ($^{35}Cl^{37}Cl$, nuclear spin $I = {}^3/_2$). The directions of the principal axes of the $^{35}Cl^{37}Cl$ ligand hfs tensors in the molecular frames commonly used for d^1 systems[29] are illustrated in Figure 2. The ligand hfs observed in the perpendicular part of the spectrum does not necessarily correspond to a principal value of the $^{35}Cl^{37}Cl$ hfs tensor.

The EPR spectra suggest an "in-plane π-type" ground state for the molecular orbital (MO) of the unpaired electron (eq 2) as

$$\psi^*_{MO}(B_2) = \beta_2|d_{xy}\rangle - \beta_2'|\phi_L\rangle \quad (2)$$

found also for the analogous Mo(V) and Re(VI) complexes $[MoOCl_5]^{2-}$ and $[ReOCl_5]^-$, respectively.[30-33] $|\phi_L\rangle$ represents a linear combination of 3p orbitals of the equatorial Cl ligands; contributions of the Cl 3s orbitals are expected to be very small according to MO calculations made for $ReOCl_4$.[33]

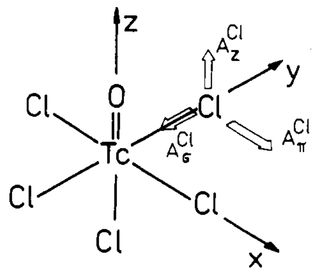

Figure 2. Directions of the principal axes of the $^{35}Cl^{37}Cl$ ligand hyperfine splitting tensors commonly used for d^1 systems.[29]

The ^{99}Tc hfs can be used to estimate the degree of covalency of the equatorial Tc–Cl bonds. Applying the formalism given by McGarvey[34]

$$A_\parallel{}^{Tc} = -K - {}^4\!/_7\beta_2{}^2P + (g_\parallel - g_e)P + {}^3\!/_7(g_\perp - g_e)P \quad (3a)$$

$$A_\perp{}^{Tc} = -K + {}^2\!/_7\beta_2{}^2P + {}^{11}\!/_{14}(g_\perp - g_e)P \quad (3b)$$

and

$$A_{av}{}^{Tc} = -K + (g_{av} - g_e)P \quad (3c)$$

where K is a measure of the Fermi contact interaction and $P = g_eg_N\beta_e\beta_N\langle r^{-3}\rangle_{4d} = 230 \times 10^{-4}$ cm^{-1}, one arrives at a value of $\beta_2{}^2 = 0.77$. $\beta_2{}^2$ is a measure of McGarvey[34] of the equatorial Tc–Cl bonds in the MO of the unpaired electron. The P value used is somewhat larger than that reported for Tc^{2+}: $P(Tc^{2+}) = 200 \times 10^{-4}$ cm^{-1}.[34] This value has been obtained considering the charge dependence of P for other transition metals.[33,35] The effective charge of Tc has been assumed to be between 2+ and 3+ as suggested by earlier studies on the corresponding Mo(V) complexes.[30-32]

Some additional information about delocalization of "unpaired spin density" can be obtained from the $^{35}Cl^{37}Cl$ hyperfine interactions. The $^{35}Cl^{37}Cl$ splitting observed in the perpendicular part of the spectrum (a) supports the presence of equatorially coordinated Cl^- ligands and (b) indicates a noticeable delocalization of spin density to these donors. However, this splitting is expected to represent a complex superposition of two seven-line patterns with splittings of $A_\pi{}^{Cl}$ and $A_\sigma{}^{Cl}$. From line-width considerations made on the ^{99}Tc hyperfine lines in the parallel part of the spectrum (minimum value $\Delta H_{pp} \approx 0.5$ mT) a value of $A_z{}^{Cl} \approx 0.4 \times 10^{-4}$ cm^{-1} can be deduced. Therefore, the $^{35}Cl^{37}Cl$ hyperfine tensors are expected to be strongly nonaxial ones; furthermore, the signs of the tensor components seem to be different ones for the individual components as found for the analogous Mo(V) complexes.[30-32] Because of the limited data quantitative conclusions have not been deduced from the $^{35}Cl^{37}Cl$ hfs.

For $[ReOCl_5]^-$ $^{35}Cl^{37}Cl$ hyperfine interactions could not be detected because of the large line widths observed in the spectra.[33] Considering the β^2 value ($\beta^2 = 0.65$) obtained for $[ReOCl_5]^-$ from the metal hyperfine data, the Re–Cl bonds seem to be remarkably more covalent in character than the Tc–Cl ones. Concerning the bonding properties, $[TcOCl_5]^-$ appears to be much closer to $[MoOCl_5]^{2-}$, for which the bonding situation was analyzed in detail by several authors.[30-32]

In addition, the ^{99}Tc hfs parameters have been analyzed by using the table of atomic parameters recently calculated by Morton and

---

[24] Kirmse, R.; Stach, J.; Abram, U.; Marov, I. N. *Z. Anorg. Allg. Chem.* **1984**, *518*, 210.
[25] Low, W.; Llewellyn, P. M. *Phys. Rev.* **1958**, *110*, 842.
[26] Maniv, S.; Bronstein, J.; Low, W. *Phys. Rev.* **1969**, *187*, 403.
[27] Römelt, G.; Schwochau, K. *Z. Naturforsch.* **1967**, *229*, 519.
[28] Bleaney, B. *Philos. Mag.* **1951**, *42*, 441.
[29] Abragam, A.; Bleaney, B. "Electron Paramagnetic Resonance of Transition Ions"; Clarendon Press: Oxford, 1970.
[30] Manoharan, P. T.; Rogers, M. T. *J. Chem. Phys.* **1968**, *49*, 5510.
[31] Van Kemenade, J. T. C. Dissertation, Delft, 1970.
[32] Marov, I. N.; Kostromina, N. A. "EPR and NMR in the Chemistry of Coordination Compounds"; Nauka: Moscow, 1979; p 138.
[33] Al-Mowali, A. H.; Porte, A. L. *J. Chem. Soc., Dalton Trans.* **1975**, 50.
[34] McGarvey, B. R. *J. Phys. Chem.* **1967**, *71*, 51.
[35] Manoharan, P. T.; Vijava, S.; Shock, J. R.; Rogers, M. T. *J. Chem. Phys.* **1975**, *63*, 2507.

Preston.[36] The analysis (neglecting second-order contributions) yields for Tc $C_s^2 = 0.0456$ and $C_d^2 = 0.69$, which corresponds to a β^2 value of $\beta^2 = 0.74$ (C_s and C_d are the Tc 5s and 4d contributions to the MO of the unpaired electron). The β^2 value is in good agreement with the one obtained above.

More insight in the bonding situation of $[TcOCl_5]^-$ and additional insight in that of the corresponding $[TcOX_5]^-$ complexes could be obtained if complexes with X = Br (the $^{79}Br^{81}Br$ hfs coupling constants are expected to be larger by a factor 4 or 5 than the $^{35}Cl^{37}Cl$ splittings because of the larger nuclear magnetic moments of $^{79}Br^{81}Br$) would be available. However, when the same reaction conditions as those used for $[TcOCl_5]^-$ were applied (using a concentrated solution of HBr instead of HCl), the formation of $[TcOBr_5]^-$ could not be detected.

Finally, it should be noted that the complex anion $[TcOCl_5]^-$ formed by the reaction of $[TcO_4]^-$ with H_2SO_4/HCl is not stable for a longer time; after 1 h the deep blue color of the solution vanishes and the intensity of the EPR signal decreases.

Acknowledgment. The authors thank Prof. Dr. I. N. Marov (Vernadsky-Institute, Academy of Sciences, Moscow) for stimulating this work.

Registry No. $KTcO_4$, 13718-33-7; $[TcOCl_5]^-$, 93558-25-9.

---

(36) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.

Contribution from the P. M. Gross Chemical Laboratory,
Department of Chemistry, Duke University, Durham, North Carolina 27706

Comparison of the Kinetics, Mechanism, and Thermodynamics of Aqueous Iron(III) Chelation and Dissociation by Hydroxamic Oxo and Thio Acid Ligands

L. LYNNE FISH and ALVIN L. CRUMBLISS*

Received July 17, 1984

The kinetics and thermodynamics of aqueous iron(III) complexation by $4\text{-}CH_3OC_6H_4C(X)N(OH)H$ (X = O, S) to form $Fe(H_2O)_4(4\text{-}CH_3OC_6H_4C(X)N(O)H)^{2+}$ are reported. These data provide a direct comparison between the iron(III) chelation chemistry of hydroxamic oxo and thio acids. A parallel-path mechanism involving $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_5OH^{2+}$ was found to be operative for both ligands. Equilibrium quotients and microscopic rate constants for the forward and reverse directions of both paths were obtained along with the corresponding ΔH°, $\Delta H^\ddagger$ and ΔS°, $\Delta S^\ddagger$ values. An associative interchange (I_a) mechanism is operative for the substitution of both ligands at $Fe(H_2O)_6^{3+}$. Data are also presented that support an I_a mechanism for substitution at $Fe(H_2O)_5OH^{2+}$, although the associative character in this path may be due to H-bonding interactions between the ligand and coordinated OH^-. Initial bond formation at iron(III) for either path occurs at the >C=X (X = O, S) site. The *thio*hydroxamic acid forms a more stable complex at physiological pH, and aquation by the acid-dependent and acid-independent paths is ca. 50 times slower than for the hydroxamic acid complex. The increased kinetic stability is consistent with enhanced delocalization of the N atom lone electron pair into the C–N bond in the thiohydroxamic acid complex. The chemistry of iron(III) chelation by $CH_3OC_6H_4C(S)N(OH)H$ suggests that siderophores may exist that use the thiohydroxamate moiety for iron(III) binding.

Introduction

Siderophores are low molecular weight sequestering agents synthesized by microbes to facilitate the solubilization and transport of iron from the environment to the cell. The structure and function of these natural chelators have been reviewed.[1–4] An important structural feature of the siderophores is the incorporation of catechol or hydroxamate groups that are capable of selectively binding iron(III) in the presence of other biologically important metal ions.[5] Synthetic catechol and hydroxamic acid chelators have been investigated as structural and kinetic models of the siderophores.[6–9] An investigation of the electronic effects influencing hydroxamic acid–iron(III) chelation kinetics and complex stability is being carried out in this laboratory.[10–12]

Closely related to the hydroxamic acids are the *thio*hydroxamic acids, $R_1C(S)N(OH)R_2$,[13] which are also capable of forming stable transition-metal complexes.[14] Cupric and ferric complexes of *N*-methylthioformohydroxamic acid have been isolated from the culture supernatant fluids of *Pseudomonas fluorescens*,[15] *Pseudomonas reptilivora*,[16] and *Streptomyces*.[17] Although the biological function of these thiohydroxamato complexes is not fully understood, they have been found to exhibit antibiotic activity,[15–18] which is a characteristic of several hydroxamic acid siderophores.[19]

---

(1) (a) Neilands, J. B. *Microbiol. Sci.* **1984**, *1*, 9. (b) Neilands, J. B. *Adv. Inorg. Biochem.* **1983**, *5*, Chapter 6. (c) Neilands, J. B. *Annu. Rev. Microbiol.* **1982**, *36*, 285. (d) Neilands, J. B. *Annu. Rev. Biochem.* **1981**, *50*, 715. (e) Neilands, J. B. In "Iron in Biochemistry and Medicine", 2nd ed.; Jacobs, A., Worwood, M., Eds.; Academic Press: New York, 1980; p 529.

(2) (a) Emery, T. *Am. Sci.* **1982**, *70* (6), 626. (b) Emery, T. *Met. Ions Biol. Syst.* **1978**, *1*, Chapter 3.

(3) (a) Raymond, K. N.; Müller, G.; Matzanke, B. F. *Top. Curr. Chem.* **1984**, *123*, 49. (b) Raymond, K. N.; Carrano, C. J. *Acc. Chem. Res.* **1979**, *12*, 183.

(4) Messenger, A. J. M.; Barclay, R. *Biochem. Educ.* **1983**, *11*, 54.

(5) Neilands, J. B.; Ratledge, C. In "Handbook of Microbiology"; Laskin, A. I., Lechevalier, H. A., Eds.; CRC Press: Boca Raton, FL, 1982; Vol. IV, p 565.

(6) (a) Raymond, K. N.; Tufano, T. P. In "The Biological Chemistry of Iron"; Dunford, H. B., Dolphin, D., Raymond, K. N., Sieker, L., Eds.; D. Reidel Publishing Co.: Boston, 1982; p 85. (b) Raymond, K. N.; Pecoraro, V. L.; Weitl, F. L. In "Development of Iron Chelators for Clinical Use"; Martell, A. E., Anderson, W. F., Badman, D. G., Eds.; Elsevier: New York, 1981; p 165. (c) Raymond, K. N.; Abu-Dari, K.; Sofen, S. R. *ACS Symp. Ser.* **1980**, *No. 119*, 133.

(7) (a) Birus, M.; Kujundzič, N.; Pribanič, M. *Inorg. Chim. Acta* **1980**, *55*, 65. (b) Kujundzič, N.; Pribanič, M. *J. Inorg. Nucl. Chem.* **1978**, *40*, 789.

(8) Kazmi, S. A.; McArdle, J. V. *J. Inorg. Nucl. Chem.* **1981**, *43*, 3031.

(9) Brown, D. A.; Chidambaram, M. B. In "Metal Ions in Biological Systems"; Sigel, H., Ed.; Marcel Dekker: New York, 1982; Vol. 14, Chapter 5.

(10) Monzyk, B.; Crumbliss, A. L. *J. Am. Chem. Soc.* **1979**, *101*, 6203.

(11) Monzyk, B.; Crumbliss, A. L. *J. Inorg. Biochem.* **1983**, *19*, 19.

(12) Brink, C. P.; Crumbliss, A. L. *Inorg. Chem.* **1984**, *23*, 4708.

(13) Walter, W.; Schaumann, E. *Synthesis* **1971**, *No. 3*, 111.

(14) Mizukami, S.; Nagata, K. *Coord. Chem. Rev.* **1968**, *3*, 267.

(15) (a) Itoh, S.; Inuzuka, K.; Suzuki, T. *J. Antibiot.* **1970**, *23*, 542. (b) Shirahata, T.; Deguchi, T.; Hayashi, T.; Matsubora, I.; Suzuki, T. *J. Antibiot.* **1970**, *23*, 546. (c) Egawa, Y.; Umino, K.; Awataguchi, S.; Kawano, Y.; Okuda, T. *J. Antibiot.* **1970**, *23*, 267.

(16) (a) Del Rio, L. A.; Gorgé, J. C.; Olwares, J.; Mayor, F. *Antimicrob. Agents Chemother.* **1972**, *2*, 189. (b) Martinez-Molina, E.; Del Rio, L. A.; Olivares, J. *J. Appl. Bacteriol.* **1976**, *41*, 69.

(17) Miyamura, S. Japanese Patent 87087, 1973.

(18) Bell, S. J.; Friedman, S. A.; Leong, J. *Antimicrob. Agents Chemother.* **1979**, *15*, 384.

(19) Neilands, J. B. *Adv. Chem. Ser.* **1977**, *No. 162*, 3.

0020-1669/85/1324-2198\$01.50/0 © 1985 American Chemical Society