A Phenoxo-Bridged Diferric Complex with Two Different Coordination Numbers in Two Distinct Coordination Sites

Catherine Belle, Isabelle Gautier-Luneau,
Jean-Louis Pierre,* and Corinne Scheer

Laboratoire de Chimie Biomimétique, LEDSS (UMR CNRS
C5616), Université J. Fourier, BP 53,
38041 Grenoble Cedex 9, France

Eric Saint-Aman

Laboratoire d'Electrochimie Organique et de Photochimie
Redox (UMR CNRS 5630), Université J. Fourier, BP 53,
38041 Grenoble Cedex 9, France

Received October 12, 1995

Introduction

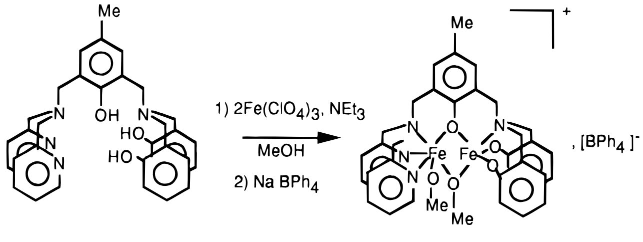
Although the metal ions in dinucleating biosites of oxo-bridged diiron proteins[1] are often in two chemically distinct environments, there are only a limited number of synthetic models in which the two coordination sites are inequivalent.[2−8]

The structural and magnetic characterization and the electrochemical study of the unsymmetrical (μ-phenoxo)(μ-methoxo)(methoxo)diiron(III) complex **1** are described herein. The complex **1**, identified as [$Fe_2L(\mu\text{-}OCH_3)(OCH_3)$]$BPh_4$], was obtained from the new unsymmetrical heptadentate ligand H_3L which involves two different complexing "arms" ((bis(2-pyridylmethyl)amino)methyl and (bis(2-hydroxyphenyl)amino)-methyl) at the *ortho* positions of *p*-cresol[9] (Scheme 1).

Experimental Section

Synthesis of [$Fe_2L(\mu\text{-}OCH_3)(OCH_3)$]$BPh_4$ (1). To a methanolic solution (5 mL) containing a mixture of 0.1 g (0.18 mmol) of H_3L and 5 equiv of triethylamine was added 2 equiv of $Fe(ClO_4)_3\cdot 9H_2O$. The initial yellow solution turned to a brown solution, which yields a brown precipitate of **1** upon addition of sodium tetraphenylborate. X−ray quality crystals were obtained by vapor diffusion of methanol into an acetonitrile/methanol solution of **1**. The crystalline complex was washed with methanol and dried under high vacuum for 7−8 h, giving a material which still contains a mixture of occluded methanol and acetonitrile, as had been observed in the crystal structure (see X-ray analysis). Elemental analysis confirms the formulation and exhibits the presence of only one counteranion in the complex, evidencing the diferric redox state. Anal. Calcd for [$Fe_2L(\mu\text{-}OCH_3)(OCH_3)$]$BPh_4\cdot 0.5CH_3CN\cdot 0.5CH_3OH$, $C_{62.5}H_{61.5}N_{4.5}O_{5.5}Fe_2B$: C, 69.11; H, 5.71; N, 5.80; Fe, 10.28. Found: C, 68.41; H, 5.79; N, 6.00; Fe, 10.20.

Scheme 1



H_3L **1**

Caution! Perchlorate salts of metal complexes are potentially explosive and should be handled in small quantities with care.

Cyclic Voltammetry Measurements. Electrochemical experiments were conducted in CH_3CN + 0.1 M Bu_4NBF_4 as supporting electrolyte, under an argon atmosphere at room temperature, using a platinum disk electrode as working electrode and a Ag/Ag^+ 10 mM + Bu_4NClO_4 0.1 M + CH_3CN electrode as reference electrode (−0.07 V *vs* ferrocinium/ferrocene couple used as internal reference in our experimental conditions).

Magnetic Susceptibility Measurements. Magnetic measurements on powder samples were carried in the range 2−300 K. The temperature dependence of the molar susceptibility χ was analyzed by using the Heisenberg spin Hamiltonian[10] $\mathbf{H} = -2JS_1\cdot S_2$ for a pair of spins $S_1 = S_2 = {}^5/_2$, by the use of the van Vleck equation with the eigenvalues of the spin-coupling Hamiltonian. The fit of the data was improved by the addition of a small amount of monomeric Fe^{III} impurity, and the temperature independent paramagnetism was also taken into account.

X-ray Data Collection and Crystal Structure Determination of [$Fe_2(C_{35}H_{36}N_4O_3)(\mu\text{-}OCH_3)(OCH_3)$]$BPh_4\cdot 0.5CH_3CH\cdot 0.5CH_3OH$. A dark brown block crystal (0.30 × 0.30 × 0.50 mm) was mounted on a Nicolet XRD four circle diffractometer using a graphite-crystal monochromator (λ(Mo Kα) = 0.710 73 Å). Cell parameters (a = 10.163(7) Å, b = 16.373(10) Å, c = 17.073(9) Å, β = 105.49(5)°) were determined by a least-squares refinement of 21 reflections within a θ range of 10−15°. More crystallographic details are given in Table 1.

A total of 5230 reflections were collected at 293 K in the range 3° $\le 2\theta \le$ 50° and were corrected for Lorentz and polarization effects but not for absorption ($\mu = 0.585\ mm^{-1}$). A total of 4955 independent reflections were used in the structural analysis. The structure was solved using an automatic Patterson procedure with the SHELXS-86 program[11] and refined against all F^2 (SHELXL-93).[12] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of the ligand and BPh_4^- counterion were generated in idealized positions and refined, riding on the carrier atoms, with isotropic thermal parameters (U(H) = 1.5U_{eq} (C) for the methyl hydrogen atoms and U(H) = 1.2U_{eq}(C) for the aromatic hydrogen atoms). The disordered solvent were correctly determined as 0.5 acetonitrile (C63−C62−N5) and 0.5 methanol (C64−O6) in the same crystallographic site occupation, according with elemental analysis and density measurement. Restraints on anisotropic displacement parameters (similar $\mathbf{U}_{ij}$ values) were applied for close atoms of disordered solvents (C62, C63 of acetonitrile and C64 of methanol; d(C64⋯C62) = 0.821 Å, d(C64⋯C63) = 0.704 Å). The molecules of solvent are hydrogen-bonded to the complex (d(N5⋯H10B) = 2.50(3) Å, C10−H10B⋯N5 = 157 (1)°; d(O6⋯H16A) = 2.62(3) Å, C16−H16A⋯O6 = 162(1)°; C10 and C16 are the carbon atoms between the pyridine cycles and the tertiary nitrogen N1).

Final cycle refinement including 703 parameters and 13 restraints converged to $R(F) = 0.045$ (for 4120 $F > 4\sigma(F)$), $R_w(F^2) = 0.115$, and restrained goodness of fit $S = 1.086$ for all 4955 $F^2[(\Delta/\sigma)\text{max} =$

---

(1) (a) Sanders-Loehr, J. In *Iron Carriers and Iron Proteins*; Loehr, T. M., Ed.; VCH: New York, 1989. (b) Wilkins, R. G. *Chem. Rev.* **1992**, 171−178.

(2) Gomez-Romero, P.; Witten, E. H.; Reiff, W. M.; Backes, G.; Sanders-Loehr, J.; Jameson, G. B. *J. Am. Chem. Soc.* **1989**, *111*, 9039−9047.

(3) Bernard, E.; Moneta, W.; Laugier, J.; Chardon-Noblat, S.; Deronzier, A.; Tuchagues, J. P.; Latour, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 887−889.

(4) Kanda, W.; Moneta, W.; Bardet, M.; Bernard, E.; Debaecker, N.; Laugier, J.; Bousseksou, A.; Chardon-Noblat, S.; Latour, J. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 588−590.

(5) Fallon, G. D.; Markiewicz, A.; Murray, K. S.; Quach, T. *J. Chem. Soc., Chem. Commun.* **1991**, 199−200.

(6) Tolman, W. B.; Liu, S.; Bentsen, J. G.; Lippard, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 152−164.

(7) Bonardi, A.; Merlo, C.; Pelizzi, C.; Pelizzi, G.; Tarasconi, P.; Cavatorta, F. *J. Chem. Soc., Dalton Trans.* **1991**, 1063−1069.

(8) Norman, R. E.; Yan, S.; Que, L.; Backes, G.; Ling, J.; Sanders−Loehr, J.; Zhang, J. H.; O'Connor, C. J. *J. Am. Chem. Soc.* **1990**, *112*, 1554−1562.

(9) Belle, C.; Gellon, G.; Scheer, C.; Pierre, J. L. *Tetrahedron Lett.* **1994**, *35*, 7019−7022.

(10) O'Connor, C. J. *Prog. Inorg. Chem.* **1979**, *29*, 204−283.

(11) Sheldrick, G. M. *Acta Crystallogr., Sect. A.* **1990**, *46*, 467−473.

(12) Sheldrick, G. M.; SHELXL93: Program for the Refinement of Crystal Structures. University of Göttingen, Germany.

S0020-1669(95)01305-X CCC: $12.00

Table 1. Crystal Data

formula: $[Fe_2(C_{35}H_{36}N_4O_3)(\mu\text{-}OCH_3)]B(C_6H_5)_4\cdot 0.5CH_3CN\cdot 0.5CH_3OH$
fw: 1087.18
cryst syst: monoclinic
$a = 10.163(7)$ Å
$b = 16.373(10)$ Å
$c = 17.073(9)$ Å
$\beta = 105.49\ (5)°$
$R(F)^a = 0.045$ [for 4120 $F > 4\sigma(F)$
no. of refined params = 703
absolute struct param$^c = -0.02(2)$
space group: $P2_1$
$V = 2737(3)$ Å^3
$Z = 2$
$D_m = 1.321$ g/cm^3; $D_x = 1.319$ g/cm^3
$F(000) = 1140$
$R_w(F^2)^b = 0.1153$ [for 4955 reflections]
restraints = 13

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. Calculated weights: $w = 1/[\sigma^2(F_o^2) + (0.0538P)^2 + 1.2925P]$ with $P = (F_o^2 + 2F_c^2)/3$. [c] Expected values for the absolute structure parameter are 0 (within 3 esd's) for correct and +1 for inverted absolute structure.

0.003, $\Delta\rho_{max} = 0.44$ e·Å^{-3}, $\Delta\rho_{min} = -0.41$ e·Å^{-3}]. The Flack absolute structure parameter[13] is equal to −0.02(2) which provides evidence that the absolute structure has been assigned correctly.

Results and Discussion

Cyclic voltammetric studies of **1** in acetonitrile show (Figure 1), in the negative region, a reversible wave at $E_{1/2} = -0.45$ V followed by a quasi-reversible wave ($E_{pa} = -1.11$ V, $E_{pc} = -1.29$ V) vs Ag/Ag$^+$ leading to the Fe^{II}Fe^{III} and Fe^{II}Fe^{II} species, respectively. The first electron transfer at −0.45 V leading to the mixed-valence complex Fe^{II}Fe^{III} likely occurs on the metallic center of the bis(pyridyl) moiety in agreement with the greater donor character of the phenolate group. Due to higher electron density resulting from the terminal phenolate groups,[14] the redox processes are significantly shifted to more cathodic potentials compared to those of other phenoxo-bridged diiron complexes in which each iron atom is bonded to two pyridyl terminal groups[15] or to one pyridyl and to one phenolate terminal groups.[3,4] On the other hand, redox potentials for **1**, which involved two distincts coordination sites, are close to the values found for the equivalent symmetrical complexes.[14,16] Compared to complexes with four pyridyl terminal groups,[15] the diiron^{III} state is stabilized by 0.85 V while the diiron^{II} form is destabilized by 0.9 V. As a consequence, the mixed-valence state of **1** and of the equivalent symmetrical complexes[14,16] have a comparable stability domain, $\Delta E_{1/2} = 0.7-0.75$ V. The stability of the Fe^{II}/Fe^{III} form of **1** toward comproportionation can be evaluated by the corresponding constant k ($\Delta E_{1/2} = (RT/F)(\ln k)$, $\Delta E_{1/2}$ is the $E_{1/2}$ separation). Using $\Delta E_{1/2} = 0.75$ V, we have determined k to be 3.2×10^{12}, indicating that mixed-valence complex forms are stabilized.

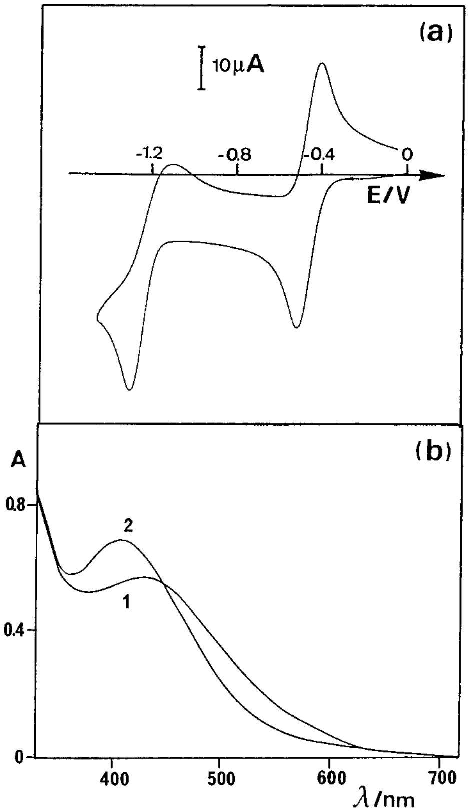


Figure 1. (a) Cyclic voltammogram of **1** (1.74 mM) in $CH_3CN + Bu_4NBF_4$ 0.1 M. Conditions: scan rate 0.1 V/s; reference electrode Ag/Ag$^+$ 10 mM + Bu_4NClO_4 0.1 M + CH_3CN. (b) UV−visible spectrum of the initial complex **1** (curve 1), of 1.03 mM **1** in $CH_3CN + Bu_4NBF_4$ 0.1 M, and after exhaustive controlled potential electrolysis at −0.75 V (curve 2). $l = 1$ cm.

After exhaustive controlled-potential electrolysis at −0.75 V, the cyclic voltammogram exhibited an additional reversible system ($E_{1/2} = -0.21$ V) with a weak intensity (the ratio of the peak intensities corresponding to the systems at −0.21 and −0.45 V is about 0.16) due to some partial ligand exchange in CH_3CN since a similar experiment carried out in CH_2Cl_2 did not show this phenomenon. Exhaustive reoxidation at 0 V of this solution fully restored the initial solution as judged by UV and electrochemical measurements, indicating the reversiblity of the decoordination−recoordination process. The second electron transfer at $E_{pc} = -1.29$ V leads to the Fe^{II}Fe^{II} form, which decomposes during electrolysis.

The main features in the electronic absorption spectrum of **1** in CH_3CN solution are the bands at 321 nm ($\epsilon \approx 9410$ L·mol^{-1}·cm^{-1}) and 438 nm ($\epsilon \approx 5610$ L·mol^{-1}·cm^{-1}). The latter band may be assigned to charge-transfer transition from a phenolate-to-Fe^{III} ion.[14] The electronic absorption of the one-electron reduced solution[17] exhibits a band at 410 nm ($\epsilon \approx 6840$ L·mol^{-1}·cm^{-1}) (Figure 1). As previously reported,[16b] this new band is the result of the overlapping of two (CT) transitions, the phenolate-to-Fe^{III} and the Fe^{II}-to-pyridine transitions in which the Fe^{II}-to-pyridine (CT) transition is shifted to higher energy with respect to the phenolate-to-Fe^{III} band.[3,15c]

Variable temperature magnetic data for a solid sample of **1** reveal a moderate antiferromagnetic interaction between the two Fe^{III} centers. Very good agreement between theory and experimental data was obtained up to 250 K by using the following parameters: $g = 2.0$, $J = -13$ cm^{-1}, % imp = 0.91, and TIP = 2.98×10^{-11} cm^3/mol.

---

(13) Flack, H. D. *Acta Crystallogr., Sect. A.* **1983**, *39*, 876−881.

(14) Neves, A.; de Brito, M. A.; Vencato, I.; Drago, V.; Griesar, K.; Haase, W.; Mascarenhas, Y. P. *Inorg. Chim. Acta* **1993**, *214*, 5−8.

(15) (a) Suzuki, M.; Oshio, H.; Uehara, A.; Endo, K.; Yanaga, M.; Kida, S.; Saito, K.; *Bull. Chem. Soc. Jpn.* **1988**, *60*, 3547−3555. (b) Borovik, A. S.; Que, L. J. *J. Am. Chem. Soc.* **1988**, *110*, 2345−2347. (c) Borovik, A. S.; Papaefthymiou, V.; Taylor, L. F.; Anderson, O. P.; Que, L. J. *J. Am. Chem. Soc.* **1989**, *111*, 6183−6195.

(16) (a) Campbell, V. D.; Parsons, E. J.; Pennington, W. T. *Inorg. Chem.* **1993**, *32*, 1773−1778. (b) Neves, A.; Erthal, S. M. D.; Drago, V.; Griesar, K. W. *Inorg. Chim. Acta* **1992**, *197*, 121−124.

(17) The electronic absorption spectrum was recorded using a diode array spectrophotometer HP 8452A through optic fiber during electrolysis performed in a glovebox in order to avoid reoxidation of the Fe^{III}/Fe^{II} form of **1** by air atmosphere.

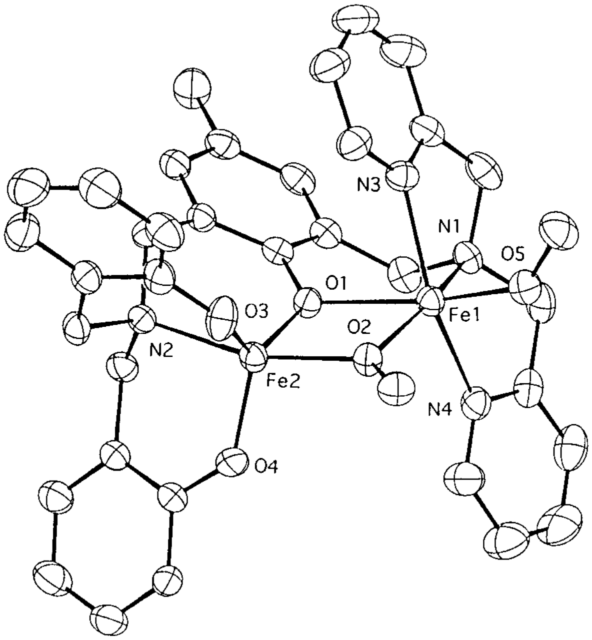


Figure 2. Thermal ellipsoid plot (30% probability ellipsoids) of the cationic part of **1** showing the numbering scheme. The hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe1−O1 2.166(4), Fe1−O2 1.938(4), Fe1−O5 1.830(5), Fe1−N1 2.183(5), Fe1−N3 2.156(5), Fe1−N4 2.145(5), Fe2−O1 1.988(4), Fe2−O2 1.975(4), Fe2−O3 1.872(5), Fe2−O4 1.850(5), Fe2−N2 2.124(5), Fe1···Fe2 3.193(2); O5−Fe1−O2 101.5(2), O5−Fe1−N4 91.7(2), O2−Fe1−N4 95.5(2), O5−Fe1−N3 92.2(2), O2−Fe1−N3 109.6(2), N4−Fe1−N3 153.1(2), O5−Fe1−O1 168.1(2), O2−Fe1−O1 73.3(2), N4−Fe1−O1 99.3(2), N3−Fe1−O1 79.9(2), O5−Fe1−N1 98.7(2), O2−Fe1−N1 158.1(2), N4−Fe1−N1 75.3(2), O4−Fe2−O3 117.2(2), O4−Fe2−O2 102.8(2), O3−Fe2−O2 92.4(2), O4−Fe2−O1 112.4(2), O3−Fe2−O1 130.4(2), O2−Fe2−O1 76.6(2), O4−Fe2−N2 92.4(2), O3−Fe2−N2 89.8(2) O2−Fe2−N2 161.5(2), O1−Fe2−N2 87.9(2), N3−Fe1−N1 77.8(2), O1−Fe1−N1 88.3(2), Fe2−O1−Fe1 100.4(2), Fe1−O2−Fe2 109.4(2).

The crystal structure of the discrete complex **1** cation (Figure 2) reveals that the two iron atoms are in distinct coordination sites with two different coordination numbers, 6 for Fe1 and 5 for Fe2. The two ferric cations are bridged by the central phenoxo and a methoxo group. The Fe1 environment is completed by a third oxygen atom from a monodentate methanolate group and one tertiary nitrogen atom and two pyridine nitrogen atoms from the L ligand. These two pyridines are trans to each other, unlike in complexes of similar ligands with two pyridines cis.[3,14,18,19] The Fe2 atom is pentacoordinated by four oxygen and one nitrogen atoms. The Fe2 coordination polyhedra is a distorted trigonal bipyramid with atoms O1, O3, and O4 forming the trigonal plane (where Fe2 is perfectly located in the plane (0.001(1) Å)). The degree of distortion Δ from an ideal trigonal bipyramid TBP ($\Delta = 0$) to square pyramid ($\Delta = 1$) according to the method of Muetterties[20] and Galy[21] is in this case equal to 0.38. The four atoms Fe1, Fe2, O1, and O2 are in the same plane with a maximal distance to the mean plane of 0.037(2) Å.

The bridged angles are relatively close, the methoxo Fe1−O2−Fe2 and phenoxo Fe1−O1−Fe2 angles are respectively 109.4(2) and 100.4(4)°, which lead together to the short distance Fe1···Fe2 of 3.193(2) Å, in the range of dibridged alkoxophenoxodiiron^{III} complexes.[5,22] The methoxo bridge is weakly asymmetric (*d*(Fe1−O2) = 1.938(4) Å, *d*(Fe2−O2) = 1.975(4) Å), while the phenoxo one is strongly (*d*(Fe1−O1) = 2.166(4) Å, *d*(Fe2−O1) = 1.988(4) Å). The unusual length of the Fe1−O1 bond can be ascribed to the structural trans effect of the short bond length Fe1−O5, 1.830(5) Å, where O5 is the oxygen of the monodentate methanolate ligand. Similar short Fe−OR bonds which decrease the affinity of the Fe for the phenolate bridge have already been observed, with other symmetrical binucleating ligands—either by a trans effect (*d*(Fe−OR) = 1.852(12) and 1.854(11) Å) where the bond length Fe−μ-O are very long (2.158(11) and 2.107(11) Å)[18] or with a Fe−OR interaction (*d* = 1.849(4)Å) which is cis to the bridging oxygen implying a shorter Fe−μ-O bond (1.975(4)Å).[19] The strong Fe−OCH3 interaction can be compared to the one in Fe^{III}(TPP)-OCH$_3$[23] (1.816(2) Å) where the authors showed (by a map of the electronic density distribution) that the hybridization of oxygen is of the sp^2 type, suggesting a π-interaction between Fe and O.

LH$_3$ is a rare example of a binucleating ligand giving a complex with two different coordination numbers in the two sites. A doubly bridged (one methoxo and one alkoxo) diferric complex containing one five-coordinated and one six-coordinated iron center had been obtained fortuitously from a symmetrical dinucleating ligand.[5] Two other fortuitous examples with two different coordination numbers have been described. One involves two identical mononucleating ligands in a triply bridged diiron^{II} complex;[6] the other involves a symmetrical binucleating ligand[7] in a diiron^{III} complex.

Further studies are in progress, concerning the possible reactivity of **1**.

Acknowledgment. We thank Doctor L. Que (University of Minnesota) for fruitful discussion and Doctor J. M. Latour from CENG (Grenoble, France) for helpful exchange of information and help for magnetization studies.

Supporting Information Available: Complete tables of crystal data and structure refinement, fractional atomic coordinates, thermal parameters, and bond lengths and angles, a structure showing the complete numbering scheme, text discussing the determination of the magnetic susceptibility data and plot of χ_M vs *T* for solid **1** (12 pages). Ordering information is given on any current masthead page.

IC951305V

---

(18) Krebs, B.; Schepers, K.; Bremer, B.; Henkel, G.; Althaus, E.; Müller-Warmuth, W.; Griesar, K.; Haase, W. *Inorg. Chem.* **1994**, *33*, 1907−1914.

(19) Holman, T. R.; Anderson, K. A.; Anderson, O. P.; Hendrich, M. P.; Juarez-Garcia, C.; Münck, E.; Que, L. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 921−923.

(20) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748−1756.

(21) Galy, J.; Bonnet, J. J.; Andersson, S. *Acta Chem. Scand.* **1979**, *A33*, 383−389.

(22) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1982**, *21*, 2444−2448.

(23) Lecomte, C.; Chadwick, D. L.; Coppens, P.; Stevens, E. D. *Inorg. Chem.* **1983**, *22*, 2982−2992.