

Structure and Properties of a Nonheme Pentacoordinate Iron(II) Complex with a Macrocyclic Triazapyridinophane Ligand

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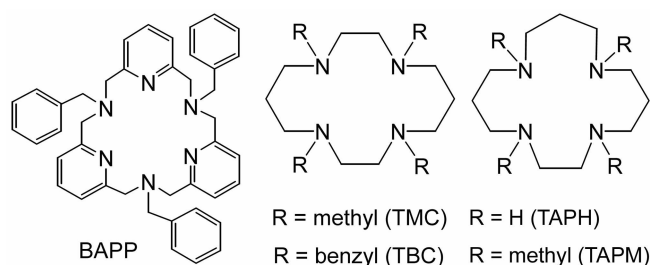
A macrocyclic ligand, *N,N',N''*-tribenzyl-2,11,20-triaza[3,3,3](2,6)pyridinophane (BAPP), was used to prepare an iron(II) complex as a nonheme model complex, $[(\text{BAPP})\text{Fe}]^{2+}$ (**1**). X-ray crystallography of a colorless crystal of **1** revealed that BAPP acted as a pentadentate ligand due to geometrical strain for the formation of a six-coordinate iron(II) complex by BAPP. As a result, the iron center revealed a significantly distorted square pyramidal geometry similar to that found in the active site of taurine dioxygenase (tauD). In the reaction of **1** with PhIO, no intermediate was observed in the UV-visible region of spectrometer at low temperatures. Catalytic oxidations of triphenyl phosphine with PhIO at -40°C revealed that **1** was able to convert triphenyl phosphine to triphenyl phosphine oxide. Thioanisole was also oxidized to the corresponding methylphenyl sulfoxide under the same conditions.

Key Words : Mononuclear iron(II) complex, Macrocyclic ligand, Nonheme, Catalytic oxidation

Introduction

Mononuclear nonheme iron centers have been often observed in the various O_2 -activation enzymes, such as lipoxygenase, α -keto acid dependent enzymes, and isopenicillin *N* synthase, and also in the antitumor drug bleomycin involved in the DNA cleavage reaction.¹⁻⁵ The common characteristics of this particular subclass of iron centers are the formation of iron(III)-peroxo and high-valent iron(IV and V)-oxo intermediates in their reaction pathways. There have been considerable efforts toward developing model nonheme iron complexes to investigate the properties of mononuclear iron intermediates proposed in the metalloenzymes and to understand their reaction mechanisms in oxidation reactions. Recently, a few stable iron(IV)-oxo species bearing N-based ligands were isolated and characterized by X-ray crystallography and spectroscopic techniques, and their reactivities were analyzed in the oxidation of sulfide, alcohol, and alkane from this lab and other research groups.⁶⁻¹⁵ We have also reported the relative reactivities of iron(III)- η^2 -peroxo, iron(III)-hydroperoxo, and iron(IV)-oxo derived from model Fe(II) complexes in the oxidation of phosphine, sulfide, and olefin as electrophilic reactions, and the deformylation of aldehyde as a nucleophilic reaction.¹⁶ Especially, iron(II) complexes bearing the TMC ligand of a planar structure provided interesting results, such as the formation of stable iron(IV)-oxo intermediates, and diverse aspects of UV-visible and resonance Raman data in the presence of solvent molecule or coordinating exogenous ligands, such as N_3^- , SCN^- , CN^- , etc, at the axial position.^{8,9,15} In the attachment of benzyl instead of methyl (TBC) and change of a ring size (TAPH and TAPM), we reported the isolation and characterization of iron(IV)-oxo species and the catalytic oxidations of organic substrates by PhIO.^{17,18}

In the continuation of such efforts to isolate mononuclear iron intermediates as models of the iron intermediates proposed in the dioxygen activations by the mononuclear iron-containing metalloenzymes, and mimic their oxygenation reactivities, we have tried to utilize a ring-size variation of macrocyclic ligands to manipulate coordination environment around iron centers. In this paper, we report the structure of a nonheme iron(II) complex, $[(\text{BAPP})\text{Fe}]^{2+}$ (**1**), bearing a cyclic triazapyridinophane ligand which is bound to the metal in a five-coordinate mode, reactions of **1** with PhIO and H_2O_2 , and reactivities in the oxidations of triphenylphosphine and sulfide.



Materials and Methods

Materials and Catalyst Preparation. All chemicals obtained from Aldrich Chemical Co. were the best available purity and used without further purification unless otherwise indicated. PhIO was prepared from iodobenzene diacetate by a literature method.¹⁹ The ligand BAPP was prepared by a literature method.²⁰

$[\text{Fe}(\text{BAPP})](\text{ClO}_4)_2$ (**1**) was synthesized under argon by stirring equimolar amounts of $\text{Fe}(\text{ClO}_4)_2$ and BAPP in CH_3CN . Colorless crystals suitable for crystallographic analysis were obtained by vapor diffusion of diethyl ether into Fe solutions at room temperature (*ca.* 70-80% yield). Complex

Table 1. Crystallographic Data for Complex **1**

1	
formular	C ₁₂ H ₁₂ Cl ₂ FeN ₆ O ₈
fw	885.57
crystal description	colorless, needle
crystal system	Monoclinic
space group	P2 ₁ /c
T (K)	293(2)
a (Å)	12.770(3)
b (Å)	12.732(4)
c (Å)	25.745(6)
α (°)	90.00
β (°)	98.889(6)
V (Å ³)	4135.8(19)
Z	4
D _{calcd.} (g cm ⁻³)	1.422
μ (cm ⁻¹)	5.54
R1 ^a	0.0641
wR2 ^b	0.1285
Goodness of fit on F^2	0.935

^aR1 = $\| \sum |F_o| - \sum |F_c| \| / \sum |F_o|$ and wR2 = $(\sum [w(F_o^2 - F_c^2)^2] / \sum [wF_o^4])^{1/2}$, where $w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$.

1 is air-stable in a solid state and also stable for at least 1 hour at 25 °C in CH₃CN. Elemental analysis calcd (%) for **1**, C₁₂H₁₂Cl₂FeN₆O₈: C 57.0, H 4.8, N 9.5; found: C 56.8, H 5.0, N 9.1.

Caution: Perchlorate salts are potentially explosive and should be handled with care.

X-ray Crystallography. **1** was characterized using X-ray diffraction. A single crystal suitable for the crystallographic analysis was attached to the tip of a glass capillary and mounted on a Siemens CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.7107$ Å) at 293 K. Data reduction and cell refinement were performed using SMART programs. Absorption corrections were carried out by the empirical method. The structure was solved by direct methods using SHELXTL V 5.0 suite of programs. Crystallographic data and experimental conditions are summarized in Table 1. All non-hydrogen atoms in the structure were subjected to anisotropic refinement, and hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters.

Catalytic Oxidation. In a typical reaction, a solution of 1 mM **1** was prepared in 3 mL of CH₃CN. After triphenylphosphine or thioanisole (200 equiv, 200 mM) was added to the solution containing the catalyst, solid PhIO (20 equiv, 20 mM) was added by bits for 10 min at room temperature. The reaction solution was stirred for an additional 20 min and then filtered through 0.45- μ M filter. The resulting solution was analyzed with GC and HPLC. Product yields were determined by comparison against standard curves prepared with known authentic samples. Decane was used as an internal standard.

Physical Methods. UV-vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer equipped with

Optostar^{DN} variable-temperature liquid-nitrogen cryostat (Oxford Instruments). Electrospray ionization mass spectra (ESI MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument. Elemental Analysis was done on a Thermo Finnigan Italia SpA (Flash EA[®] 1112) CHN analyzer. ¹H NMR spectra were recorded on Varian Unity 500 spectrometer at ambient temperature. Chemical shifts (ppm) were referenced to the residual protic solvent peaks. Electrochemical studies were carried out with a CH instrument electrochemical analyzer (CH Inc., UK) using 0.1 M Bu₄NClO₄ in acetonitrile as the supporting electrolyte. Cyclic voltammograms (CV) were obtained with a scan rate of 100 mV/s by using a three-component system consisting of a Pt wire working electrode and silver wires as auxiliary and reference electrodes. The potential values were corrected to the SCE standard by assigning the ferrocene/ferrocenium couple as the external standard (E_{1,2}(Fc^{+1/0}) = 480 mV under the same conditions). Product analysis for the oxidation of sulfide and triphenyl phosphine was performed on Agilent Technologies 6890N gas chromatograph (GC).

Results and Discussion

In a reaction of Fe(ClO₄)₂ with BAPP in CH₃CN, the ligand was expected to coordinate to the metal in a hexadentate mode *via* its three amine nitrogens and three pyridine nitrogens. However, according to the X-ray structure of [Fe(BAPP)]⁻² (**1**), the ligand acted as a pentadentate donor with one of the amine nitrogens uncoordinated, due to a ring strain derived from the macrocyclic structure (Figure 1). The sixth coordination site was unoccupied and even not allowed for an acetonitrile molecule which was the solvent for crystallization, even though solvent molecules or counter anions were found in the rest of the coordination sites of the nonheme mononuclear Fe(II) complexes of other tetradentate and pentadentate N-rich ligands.^{18,21-26} The two Fe-N_{amine} bonds (2.330 and 2.278 Å) in **1** are longer than the

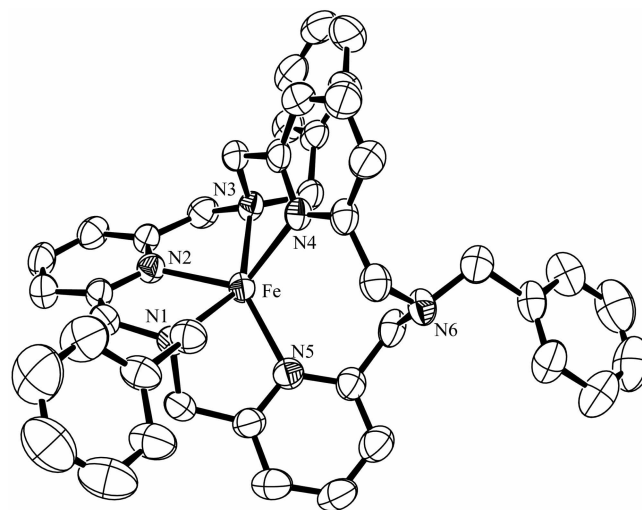


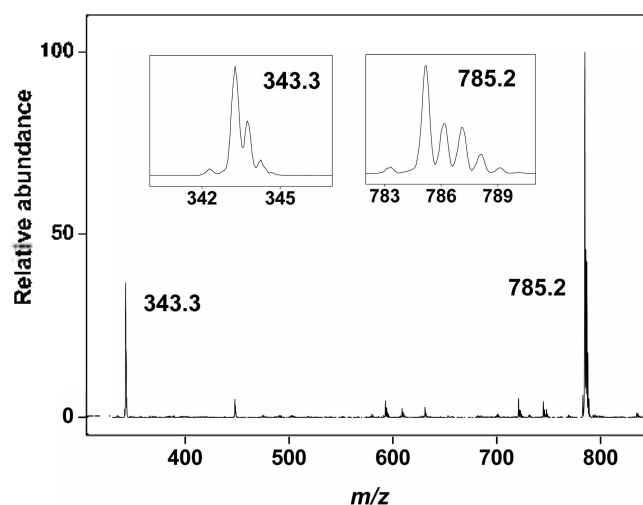
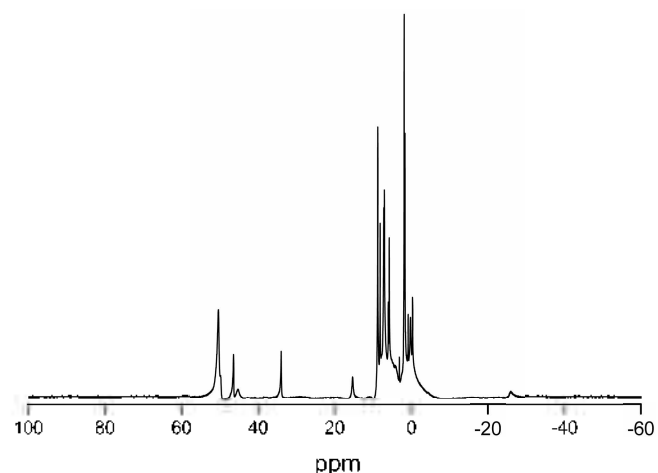
Figure 1. ORTEP plots for [Fe(BAPP)](ClO₄)₂ (**1**) showing 50% probability ellipsoids. Hydrogen atoms omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for **1**

1	
Fe-N1	2.330(3)
Fe-N2	2.131(3)
Fe-N3	2.278(3)
Fe-N4	2.234(3)
Fe-N5	2.139(4)
N1-Fe-N2	73.68(13)
N1-Fe-N3	143.88(12)
N1-Fe-N4	109.54(12)
N1-Fe-N5	74.09(13)
N2-Fe-N3	74.26(12)
N2-Fe-N4	120.99(13)
N2-Fe-N5	132.48(13)
N3-Fe-N4	74.03(12)
N3-Fe-N5	141.62(13)
N4-Fe-N5	102.27(13)

three Fe-N_{py} bonds (2.131, 2.234, and 2.139 Å), reflecting pyridine a stronger ligand for iron(II) centers (Table 2). These bond lengths of Fe-N in **1** were longer than those found for the low-spin Fe(II) complexes such as [(TPA)Fe(CH₃CN)₂]^{-2,22}, [(N4Py)Fe(CH₃CN)]^{-2,23,24}, [(TACNPy2)Fe(CH₃CN)]^{-2,27}, [(phen)₃Fe]^{+2,28} and [(bpy)₃Fe]^{-2,29} (TPA = tris(2-pyridylmethyl)amine, N4Py = *N,N*-bis(2-pyridylmethyl)-bis(2-pyridyl)methylamine, TACNPy2 = 1,4-dimethyl-7-bis(2-pyridyl)methyltriazacyclononane, phen = 1,10-phenanthroline, bpy = 4,4'-bipyridine), but analogous to those found for the high-spin Fe(II) complexes such as [(6-Me₃-TPA)Fe(CH₃CN)₂]^{+2,22}, [(6-Me₂-BPMEN)Fe(OTf)₂]⁻²⁶ and etc²⁵ (6-Me₃-TPA = tris(6-methyl-2-pyridylmethyl)amine, 6-Me₂-BPMEN = *N,N'*-dimethyl-*N,N'*-bis(6-methyl-2-pyridylmethyl)-1,2-diaminoethane). Compared to the Fe-N bond lengths in the high-spin complex, [(6-Me₃-TPA)Fe(CH₃CN)₂]⁺², the Fe-N_{py} bond lengths of **1** are similar but the coordinated amine nitrogens become more distant from the iron center because of a geometric reason caused by the stronger coordination of the three pyridines of BAPP. Expected from its solid-state structure, the complex **1** maintained its spin state in CH₃CN solution as determined by ¹H-NMR spectroscopy. Unlike the NMR spectra of the low-spin complexes, **1** afforded a spectrum typical of a high-spin Fe(II) complex with the peaks paramagnetically shifted over a range of -30 to +60 ppm (Figure 3), which was also observed in those of other mononuclear pentadentate Fe(II) complexes.³⁰

As the result of the ring strain, the iron center of **1** had a distorted square pyramidal coordination geometry ($\tau = 0.19$), similar to the geometry of the iron(II) center in TauD ($\tau = 0.12$) (Table 3). In the study of model complexes of α -keto-glutarate-dependent dioxygenases, the crystal structures of five-coordinate iron(II) centers with a trispirazoyl borate ligand and a chelated carboxylate ligand showed a range from a distorted trigonal bipyramidal to a distorted square pyramidal coordination ($\tau = 0.78$ to 0.17).³⁰ Such a low τ value found in **1** has never been known in iron(II)

**Figure 2.** Electrospray ionization mass spectrum of **1**. Inset shows observed isotope distribution patterns for ions at m/z of 343.3 and 785.2.**Figure 3.** ¹H NMR spectrum of [Fe(BAPP)](ClO₄)₂ (**1**) in CD₃CN at room temperature.

complexes with such a five-coordinate chelate ring ligand.

Bond valence sum (BVS) has been used to determine the oxidation state of metal ions in solids, metalloenzymes, and model complexes.³¹⁻³³ It was reported that the BVS values calculated from crystallographic distances predicted the oxidation state of the metal centers in different coordination numbers, with the error < 0.25 units. When the BVS value was calculated for **1** by the reported method in order to see whether the calculated value correctly verified the oxidation state of **1** with such a distorted structure, the value turned out 1.66 (Table 3), suggesting that this calculation still gave a hint for the oxidation state of **1**, but the value deviated significantly from the real oxidation state.

Further information derived from the positive ion electro-spray mass spectrum of the CH₃CN solution of **1**, which revealed ion clusters with m/z 785.2 corresponding to {[Fe(BAPP)](ClO₄)}⁻ and m/z 343.3 corresponding to {Fe(BAPP)}⁺² (Figure 2). Then, electrochemical properties of **1** were examined by the cyclic voltammetry of an

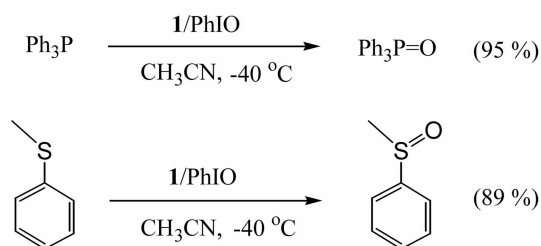
Table 3. Structural Properties of Complex **1** and Comparison with Reported Mononuclear Fe(II) and Fe(III) Complexes of a Pentadentate Coordination

	Fe-N (ave)	τ	BVS	coordi- nation
[Fe(BUA)(OH)] ⁻	2.141	0.90	2.93	1O, 4N
[Fe(Tp ^{Bu,Pr})(BF)]	2.134	0.78	1.81	2O, 3N
[Fe(Tp ^{Ph2})(PRV)]	2.119	0.67	1.89	2O, 3N
[Fe(Tp ^{Ph2})(OBz)]	2.142	0.65	1.82	2O, 3N
[Fe(Tp ^{Ph2})(BF)]	2.114	0.65	1.93	2O, 3N
[Fe(Tp ^{Ph2})(OAc)(3,5-Ph ₂ pzl)]	2.141	0.32	1.90	2O, 3N
[Fe(BAPP)] ⁺² (1)	2.222	0.19	1.66	5N
[Fe(Tp ^{Ph2})(OAc)]	2.123	0.17	1.89	2O, 3N
TauD	2.19	0.12	1.97	3O, 2N

Abbreviations: Tp^{Bu,Pr} = hydrotris(3-*tert*-butyl-5-isopropylpyrazol-1-yl)borate; Tp^{Ph2} = hydrotris(3,5-diphenylpyrazol-1-yl)borate; BUA = tris-[(*N*-*tert*-butylureaylato)-*N*-ethyl]aminato; BF = benzoylformate; PRV = pyruvate. According to this definition, a perfect square pyramid would have a τ value of 0.00, and a trigonal bipyramid would have a τ value of 1.00.^{34,35} The BVS for a given metal center can be determined using values for r_i , tabulated in ref.³¹

anaerobic acetonitrile solution with tetrabutylammonium perchlorate as the supporting electrolyte. Complex **1** showed an irreversible cyclic voltammogram with $E_{1/2} = 860$ mV vs SCE, which was comparable to those of other high-spin iron(II) complexes, such as [(6-Me₃-TPA)Fe(CH₃CN)₂]⁺², [(6-Me₂-TPA)Fe(CH₃CN)₂]⁺²,²² and the pentacoordinate iron(II) complexes bearing pyrazolylborate and benzoyl formate, ranging from 890 to 1010 mV (vs SCE).³⁰

Then, we made efforts to isolate unstable Fe intermediates by treating PhIO and H₂O₂ at low temperatures. No intermediate was observed in the UV-visible region of the spectrometer even at -40 °C, probably due to the stability of the intermediates. The ability of **1** to mediate the oxygen transfer from PhIO to phosphine was examined using triphenylphosphine as the substrate. In the reaction, 1.0 mM **1** was treated with 20 mM PhIO (20 equiv) in the presence of 0.2 M triphenylphosphine (200 equiv) in CH₃CN at -40 °C.



Product analysis of the reaction mixture revealed that triphenylphosphine oxide was yielded quantitatively (98% based on the oxidant used), demonstrating that **1** was capable of oxygenating the phosphine to the corresponding oxide product. Under the same reaction conditions only in the absence of **1**, a trace amount of the oxide product was observed. We also carried out the oxidation of thioanisole by using PhIO in CH₃CN at -40 °C: methylphenyl sulfoxide

was obtained in a high yield (89%), demonstrating that **1** was a good catalyst transferring the oxygen of PhIO to sulfide.

In summary, we have reported the preparation of the iron(II) complex **1** bearing the macrocyclic ligand, showing the significantly distorted square pyramidal structure arising from the geometrical reason. **1** and PhIO were capable of catalyzing the oxidations of triphenylphosphine and sulfide. This insight may allow for the rational design of new iron complexes as good models and for oxidation catalysts.

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References

- Borovik, A. S. *Acc. Chem. Res.* **2005**, *38*, 54.
- Neidig, M. I.; Solomon, E. I. *Chem. Commun.* **2005**, 5843.
- Abu-Omar, M. M.; Loaiza, A.; Hontzas, N. *Chem. Rev.* **2005**, *105*, 2227.
- Decker, A.; Solomon, E. I. *Curr. Opin. Chem. Biol.* **2005**, *9*, 152.
- Kryatov, S. V.; Rybak-Akimova, E. V. *Chem. Rev.* **2005**, *105*, 2175.
- Martinho, M.; Banse, F.; Bartoli, J.-F.; Mattioli, T. A.; Battioni, P.; Homer, O.; Bourcier, S.; Girerd, J.-J. *Inorg. Chem.* **2005**, *44*, 9592.
- Balland, V.; Charlot, M.-F.; Banse, F.; Girerd, J.-J.; Mattioli, T. A.; Bill, E.; Bartoli, J.-F.; Battioni, P.; Mansuy, D. *Eur. J. Inorg. Chem.* **2004**, 301.
- Bukowski, M. R.; Koehntop, K. D.; Stubna, A.; Bominaar, F. I.; Halfen, J. A.; Munck, E.; Nam, W.; Que, L., Jr. *Science* **2005**, *310*, 1000.
- Sastri, C. V.; Seo, M. S.; Park, M. J.; Kim, K. M.; Nam, W. *Chem. Commun.* **2005**, 1405.
- Sastri, C. V.; Park, M. J.; Ohta, T.; Jackson, T. A.; Stubna, A.; Seo, M. S.; Lee, J.; Kim, J.; Kitagawa, T.; Munck, E.; Que, L. J.; Nam, W. *J. Am. Chem. Soc.* **2005**, *127*, 12494.
- Oh, N. Y.; Suh, Y.; Park, M. J.; Seo, M. S.; Kim, J.; Nam, W. *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 4235.
- Klinker, E. J.; Kaizer, J.; Brennessel, W. W.; Woodrum, N. L.; Cramer, C. J.; Que, L. J. *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 4235.
- Kim, S. O.; Sastri, C. V.; Seo, M. S.; Kim, J.; Nam, W. *J. Am. Chem. Soc.* **2005**, *127*, 4178.
- Kaizer, J.; Klinker, E. J.; Oh, N. Y.; Rohde, J.-U.; Song, W. J.; Stubna, A.; Kim, J.; Munck, E.; Nam, W.; L. Que, J. *J. Am. Chem. Soc.* **2004**, *126*, 472.
- Rohde, J.-U.; In, J.-H.; Lim, M. H.; Brennessel, W. W.; Bukowski, M. R.; Stubna, A.; Munck, E.; Nam, W.; L. Que, J. *Science* **2003**, *299*, 1037.
- Park, M. J.; Lee, J.; Suh, Y.; Kim, J.; Nam, W. *J. Am. Chem. Soc.* **2006**, *128*, 2630.
- Seo, M. S.; Jang, H. G.; Kim, J.; Nam, W. *Bull. Kor. Chem. Soc.* **2005**, *26*, 971.
- Suh, Y.; Seo, M. S.; Kim, K. M.; Kim, Y. S.; Jang, H. G.; Tosha, T.; Kitagawa, T.; Kim, J.; Nam, W. *J. Inorg. Biochem.* **2006**, *100*, 627.
- Saltzman, H.; Sharefkin, J. G. *Organic Syntheses*; Wiley: New York, 1973; p 658.

20. Bottino, F.; de Grazia, M.; Finocchiaro, P.; Frinzeck, F. R.; Mamo, A.; Pappalardo, S. *J. Org. Chem.* **1988**, *53*, 3521.
 21. Bukowski, M. R.; Comba, P.; Limberg, C.; Merz, M.; Que, L. J.; Wistuba, T. *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 1283.
 22. Zang, Y.; Kim, J.; Dong, Y.; Wilkinson, E. C.; Appelman, E. H.; Que, L. J. *J. Am. Chem. Soc.* **1997**, *119*, 4197.
 23. Roelfes, G.; Lubben, M.; Chen, K.; Ho, R. Y. N.; Meetsma, A.; Genseberger, S.; NHermant, R. M.; Hage, R.; Mandal, S. K.; Young, J. V. G.; Zang, Y.; Koojiman, H.; Spek, A. L.; Que, L. J.; Feringa, B. L. *Inorg. Chem.* **1999**, *38*, 1929.
 24. Lubben, M.; Meetsma, A.; Wilkinson, E. C.; Feringa, B. L.; Que, L. J. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1512.
 25. Chen, K.; Que, L. J. *J. Am. Chem. Soc.* **2001**, *123*, 6327.
 26. Chen, K.; Costas, M.; Kim, J.; Tipton, A. K.; Que, L. J. *J. Am. Chem. Soc.* **2002**, *124*, 3026.
 27. Roelfes, G.; Vraymasu, V.; Chen, K.; Ho, R. Y. N.; Rohde, J.-U.; Zondervan, C.; La Crois, R. M.; Schudde, E. P.; Lutz, M.; Spek, A. L.; Hage, R.; Feringa, B.; Munck, E.; Que, L. J. *Inorg. Chem.* **2003**, *42*, 2639.
 28. Zalkin, A.; Templeton, D. H.; Ueki, T. *Inorg. Chem.* **1973**, *12*, 1641.
 29. Posse, G. M. E.; Juri, M. A.; Aymonino, P. J.; Piro, O. E.; Negri, H. A.; Castellano, E. E. *Inorg. Chem.* **1984**, *23*, 948.
 30. Mehn, M. P.; Fujisawa, K.; Hegg, E. L.; Que, L. J. *J. Am. Chem. Soc.* **2003**, *125*, 7828.
 31. Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.
 32. Whangbo, M.-H.; Torardi, C. C. *Science* **1990**, *249*, 1143.
 33. Thorp, H. H. *Inorg. Chem.* **1992**, *31*, 1585.
 34. O'Sullivan, C.; Murphy, G.; Murphy, B.; Hathaway, B. *J. Chem. Soc., Dalton Trans.* **1999**, 1835.
 35. Addison, A. W.; Nageswara Rao, T.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.
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