Hypothesis for Structure and Oxidation State of Manganese Cluster in Oxygen-Evolving Center Deduced from Their Magnetic Properties

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Based on the investigations for the magnetic interaction in the synthetic binuclear manganese compounds of μ-oxo bridge and for results by magnetic measurements and EXAFS studies on the native enzyme, it was concluded that there are two dimeric manganese units in the oxygen-evolving center of the photosystem II. One of them is a di-μ-oxo-bridged dimer with Mn–Mn distance of 2.7 Å, and it has a $Mn_2(III/III)$ oxidation state in both the S_1- and S_2-states. A second binuclear unit, which we will call as X-pair, is assumed to have a $Mn_2(II/III)$ oxidation state in the S_1-state, and is oxidized in the S_1- to S_2-state transition. The multiline ESR signal observed for the S_2-state has been attributed to be due to a partially oxidized ($Mn_2(III/IV)$ oxidation state) of the 2.7 Å-pair, which should be formed through the interaction between the 2.7 Å-pair with $Mn_2(III/III)$ state and the X-pair of $Mn_2(III/III)$ which is generated in the S_1- to S_2-state transition.

Introduction

The oxidation of water by photosynthetic organisms results in the releasing of molecular oxygen into the atmosphere, a process on which all animal life is dependent. The other products of water oxidation are hydrogen ion (H^+) and electron (e^-), of which there are four of each for every molecule of oxygen produced (*cf.* Eqn. (1)). The hydrogen

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{1}$$

ions and electrons thus produced do not combine to form molecular hydrogen but reduce atmospheric carbon dioxide to organic compounds. A common biochemical apparatus appears to be responsible for catalyzing this fundamental process from the most primitive cyanobacteria to all known plants. The biochemical apparatus has two parts, a photoactive reaction center membrane-protein complex termed photosystem II (PS II) and a tightly associated oxygen-evolving center (OEC) [1–4].

In photosynthesis, the primary photochemical reaction produces a strong oxidant that is not capable of directly catalyzing the four-electron oxidation of water. Instead this is accomplished by a complex comprised of four manganese ions believed to be associated in the form of a ligand-bridged cluster that serves as a storehouse for the oxidizing equivalents and as the apparent substrate-binding site.

The oxygen-evolving center (OEC) is thought to exist in five different oxidation states, so-called S-states, S_0–S_4 [5]. S_0 is the most reduced state, and the more oxidized states are formed by successive electron transfer to the photooxidized primary electron donor P680$^+$. Four consecutive charge separations are needed for the formation of one oxygen molecule. S_0 and S_1 were observed to the stable states in the dark, and in most materials the dark population of the S-states has been found to be 75% S_1 and 25% S_0 or after very long dark incubation 100% S_1 [6, 7]. The oxygen molecule is formed in the S_3–S_4–S_0 transition in which S_4 is assumed to be very short-lived.

Many different spectroscopic techniques have been applied in order to probe the chemical nature of the Mn cluster and to determine the redox changes that accompany each S-state transition. These methods include ESR, optical, X-ray absorption edge, and EXAFS spectroscopies. In addition, S-state-dependent changes in the water proton relaxation rate have been observed in the NMR measurements. A picture has emerged from ESR and X-ray absorption studies of PS II from spinach in which the Mn catalyst is a cluster containing two to four Mn atoms which are primary Mn(III) and/or Mn(IV). The first spectroscopic signature of Mn associated with an S-state arose

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from the S_2-state and was an ESR signal centered at $g = 2$ with 16–19 hyperfine lines, called multiline signal [8]. This signal is similar to the ESR spectra of a variety of binuclear Mn_2(III/IV) mixed-valence complexes with $S = 1/2$ ground state [9, 10]. A second ESR signal at $g = 4.1$ was subsequently discovered and assigned as a Mn species in the S_2-state [11–13]. This signal resembles ESR spectra from the $S = 3/2$ state of axially distorted Mn(IV) monomeric inorganic compounds [14]. The results by the EXAFS and X-ray absorption studies are summarized as follows. (a) The best fit parameters obtained from the Mn edge EXAFS data on S_1-state indicate that each Mn is coordinated to 3.25 N or O ligand atoms at a distance of approximately 1.98 Å, 2.27 N or O ligand atoms approximately 1.75 Å, and 0.68 Mn atom approximately 2.69 Å. These data have been interpreted to suggest a presence of di-μ-oxo-bridged binuclear Mn_2-unit, and are not consistent with a symmetric tetranuclear cluster, and indicate (b) an average valence between Mn(III) and Mn(IV), (c) an oxidation of Mn by 1–2 equivalent per reaction center in the S_1 to S_2 transition, which confirmed a redox role for Mn in water oxidation, and (d) no apparent changes in structure in the S_1 to S_2 transition [15, 16]. Recent refinement of the EXAFS data indicate the possible presence of additional Mn atoms separated by 3.3 Å from the dinuclear pair (2.7 Å-pair), either as (i) two "monomeric" sites, or (ii) an additional Mn_2-unit yielding a "dimer-of-dimer", separated by approximately 3.3 Å.

Very recently changes in magnetic susceptibility produced by single-turnover flashes of light have been measured for four of the oxidation states produced during oxygen evolution in spinach PS II [17]. The large increase in magnetic susceptibility was observed for the S_1 to S_2 transition, and this behaviour is apparently opposite in sign to the decrease in paramagnetism reported for the oxidation of synthetic Mn dimers containing μ-oxo-di-μ-carboxylato and di-μ-oxo-μ-carboxylato bridges undergoing the oxidation of $Mn_2(III/III) \rightarrow Mn_2(III/IV)$.

As described above there are many investigations on the structure and the role of manganese ions in the oxygen-evolving center [1–4], however, the details on the Mn cluster is still totally unknown, and at present there is no model which can comprehensively explain the magnetic properties of the Mn cluster in PS II. In this article we wish to propose a new hypothesis on the structure and the oxidation state of the Mn cluster, which is deduced from the detailed elucidation of the magnetic properties of the Mn cluster, especially the results by Dismukes *et al.* [17] and the ESR spectral properties observed for the S_2-state.

Magnetism in Polynuclear Manganese Compounds

Usually manganese ions exist in high-spin type Mn(II), Mn(III), and Mn(IV) compounds, and thus have five, four, and three unpaired electrons, respectively. The result by Dismukes *et al.* [17] clearly implies that the manganese ion which participates in the oxidation step from S_1- to S_2-state, does not exist as a "monomeric" unit, since this would give the decrease of the magnetic susceptibility on this process. There are several mechanisms that could produce the large increase in paramagnetism observed for S_1- to S_2-state, and the most plausible one is to assume that the manganese ion which is oxidized in S_1- to S_2-state is magnetically coupled with another manganese, and that the electronic coupling between manganese ions within a chemically discrete cluster decreases upon removal of an electron. This indicates that it is very important to understand the detailed nature on the electronic coupling in polynuclear Mn cluster in order to elucidate the magnetic behaviours of Mn cluster in PS II, but such studies are much limited at present. At first we will consider the magnetic interaction in synthetic polynuclear manganese compounds.

When two paramagnetic transition metal ions are present in the same molecular entity, the magnetic properties can be usually different from the sum of the magnetic properties of each ion. These compounds are generally categorized according to their magnetic behaviour into three groups depending on the strength of metal–metal interaction. In the non-interacting type, the magnetic properties of the dimer (or polymer) are essentially unchanged from the paramagnetic monomer. In the strongly interacting type, formation of relatively strong metal–metal bonds occur, and the molecule will display simple diamagnetic behaviour (for even numbers of electrons) [18].

In the present cases, the weakly-interacting metal ions are the main problem. In such compounds this weak coupling between the electrons of two metal ions leads to low-lying excited states of different spin which can be populated at thermal energies. The resulting magnetic behaviour will be antiferromagnetic or ferromagnetic depending on whether the low-spin (spin-paired) or high-spin (spins parallel) state is ground state, respectively. These interactions – often termed superexchange because of the large distances involved (3–4 Å) between the metal ions – have been observed for many compounds [19].

In experimental studies the magnetic interaction between spin S_a and S_b for atoms A and B, is usually written in a form suggested originally by Heisenberg, Dirac, and Van Vleck [20];

$$\mathcal{H} = -2JS_a \cdot S_b \tag{2}$$

where the coupling constant J is positive if the spins are parallel (ferromagnetic), and negative if they are paired (antiferromagnetic). Thus, the complete understanding on J (sign and magnitude) is very important to elucidate the magnetic behaviour of the polynuclear compounds.

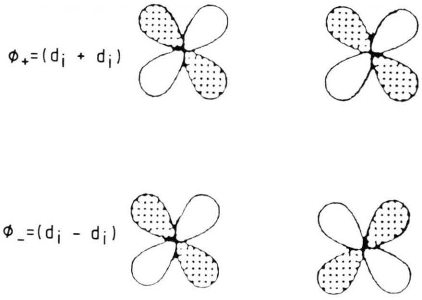
The studies on magnetic polynuclear complexes started in 1952, when Bleaney and Bowers demonstrated that the magnetism and ESR properties of copper(II) acetate were due to the dimeric nature of the molecule [19]. Many researchers then attempted to rationalize the sign and the value of J in the light of the structural data for polymeric copper(II) compounds. The most elegant of these correlations was established by Hatfield and Hodgson [21] who showed that the magnitude of the interaction in planar di-μ-hydroxo-bridged copper(II) dimer complexes depends on the Cu-O-Cu angle. Hoffmann *et al.* have made the first real semiquantitative approach to this problem [22] and a quite similar approach was also proposed by Kahn *et al.* which leads to a slightly different expression of the theoretical calculation [23]. Although some authors have criticized these approaches [24], the "orbital model" by Hoffmann and Kahn *et al.* was proved to be valid by the Nishida's result that both "complementary" and "countercomplementary" effects are observed for several binuclear copper(II) compounds [25]. This leads to the conclusion that we can discuss the magnetic interaction of synthetic polynuclear manganese compounds in term of the "orbital model". According to Hoffmann *et al.*, J in Eqn. (2) is written as the summation of J_{AF} and J_F (Eqn. (3)),

$$-J = J_{AF} - J_F \tag{3}$$

and J_{AF} and J_F are written as follows [22];

$$\begin{aligned} J_F &= 1/m^2 \sum_{i \varepsilon A} \sum_{j \varepsilon B} K_{ij} \\ J_{AF} &= 1/m^2 \sum_{i=1}^{m} \frac{1/2(\varepsilon_{2i}-\varepsilon_{2i-1})^2}{J_{ai,ai} - J_{ai,bi}} \end{aligned} \tag{4}$$

for dimeric metal(d^n) complexes with m unpaired electrons on each metal atom, where J_F is due to the electrostatic repulsion energy between two electrons in magnetic orbital, and J_{AF} is due to the superexchange (or direct) interaction described above. In Eqn. (4), ε_{2i} and ε_{2i-1} represent the energies of following orbitals, $\varnothing_+$ and $\varnothing_-$, which are linear combinations of two d orbitals, as illustrated below. The most important point is that J has a negative value (antiferromagnetic interaction) only when the energy gap between two orbitals, $\varnothing_+$ and $\varnothing_-$ is large, because J_F is always positive.



Until now several polynuclear manganese compounds have been prepared and characterized, however few systematic investigations are reported on their magnetic interaction. The manganese compounds prepared hitherto can be classified into four groups, *i.e.*,

(i) binuclear complexes with di-μ-oxo bridge [26–33]; in this case the Mn-Mn distances are very short (2.68–2.75 Å) and strong antiferromagnetic interaction is observed,

(ii) compounds with (μ-oxo)(bis-μ-acetato) core; Mn-Mn distances are in the range 3.0–3.3 Å [34–36],

(iii) compounds with di-μ-alkoxo bridg; Mn-Mn distances are in the range 2.9–3.1 Å [37],

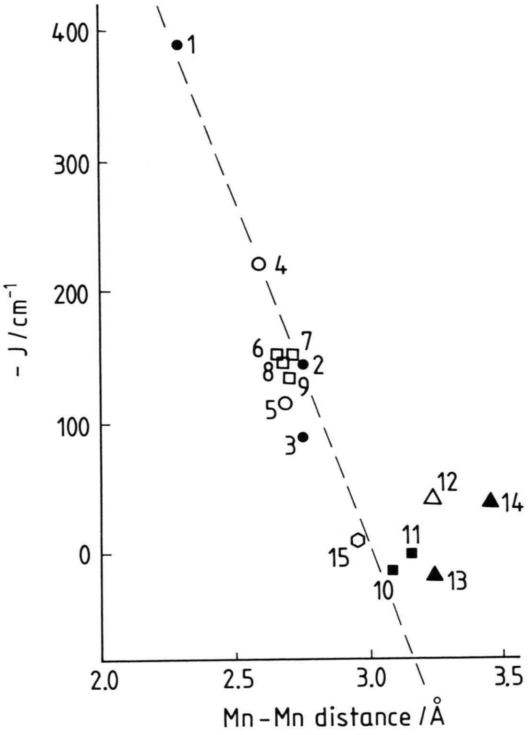


Fig. 1. The $-J$ values and Mn-Mn distances of the compounds

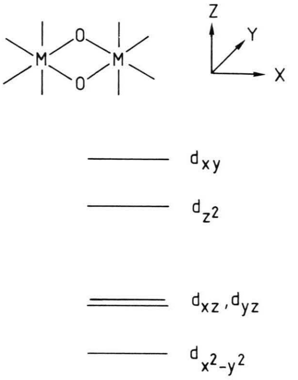
- ● di-μ-oxo Mn_2^{4+}-pairs. 1; ref. [26]; 2, ref. [27]; 3, ref. [28];
- ○ di-μ-oxo-μ-acetato Mn_2(III/IV) pair: 4, ref. [29]; 5, ref. [30];
- □ di-μ-oxo Mn_2(III/IV) pair: 6, ref. [31]; 7, ref. [32]; 8, ref. [10]; 9, ref. [27];
- ■ di-μ-acetato-μ-oxo Mn_2(III/III) pair: 10, ref. [34]; ref. [35];
- △ di-μ-acetato-μ-oxo Mn_2(III/IV) pair: 12, ref. [36];
- ▲ tetranuclear Mn_4(IV) compounds: 13, 14, ref. [39];
- ⬡ di-μ-alkoxo Mn_2(III/III) pair: 15, ref. [37].

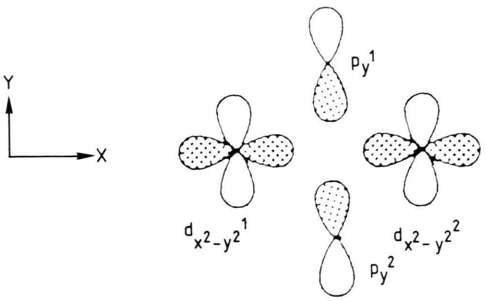
(iv) tetranuclear compounds with Mn_4-unit, and others containing more than four Mn atoms [38−41].

Fig. 1 shows the relationship between J-value and the Mn-Mn distance for several compounds whose structures were determined by the X-ray analysis. This figure demonstrates very important facts, *i.e.,*

(1) for the di-μ-oxo compounds (including those of (di-μ-oxo)(μ-acetato) core and tri-μ-oxo core), $-J$ value changes linealy with the Mn-Mn distance, and this feature is not dependent on the oxidation state of manganese ion, and

(2) $-J$ values of the compounds 10−14 of (μ-oxo)-bis(μ-acetato) and μ-oxo bridge, deviate from this lineality.





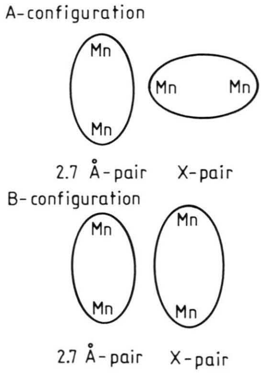
At first we will consider the magnetism of binuclear compounds with di-μ-oxo bridge. In these compounds the Mn-oxo bonds are much stronger than any other Mn-ligand bonds (N or O atom, *cf.* ref. [10]). Then the d-orbital splitting scheme for each metal ion may be roughly written as below. It should be noted here that in the Mn(III) and Mn(IV) complexes no electron is present in the d_{xy}-orbital whose lobes are directed to the oxo atoms. Thus, strong antiferromagnetic interaction through the d_{xy}-oxygen-d_{xy} path, which is frequently observed for the binuclear Fe(III) compounds with μ-oxo bridge [42], is not anticipated for these cases. This is suggesting that the direct interaction between $d_{x^2-y^2}$ orbitals (as illustrated below) is the main contribution for the large antiferromagnetism observed for binuclear manganese compounds with di-μ-oxo bridge [37], which can be rationalized in terms of the "orbital model". Above discussion leads to the important conclusion that strong antiferromagnetism is always anticipated for the di-μ-oxo bridged binuclear Mn_2 (III/III), Mn_2(III/IV), and Mn_2(IV/IV) compounds if the Mn-Mn distance is within 2.7 Å.

New hypothesis for structure and oxidation state of manganese cluster in PS II

At first we want to attach importance to the fact that all the EXAFS data indicate that no apparent change occurs in structure in the S_1 to S_2 state transition, that is, the 2.7 Å-pair is present in both the S_1- and the S_2-state. On the basis of the above fact and the results by Dismukes *et al.* [17], we can conclude that in addition to the dimeric Mn-pair with 2.7 Å, an another binuclear Mn pair should exist in OEC, the reason being as follows; (1) large increase ($\mu_{eff}^2 \sim 17$) in magnetic susceptibility observed for the S_1 to S_2 transition should not to be due to the oxidation of Mn ion of the 2.7 Å Mn-pair, because strong antiferromagnetic interaction is expected for all the dimeric Mn-pair within 2.7 Å as described before, and (2) large increase of magnetic susceptibility cannot be explained by the oxidation of any monomeric Mn ion.

Thus, we must assume the presence of two dimeric Mn_2-pairs (2.7 Å and X-pair) in OEC. There are two configurations for this model as illustrated below, although the intermediate configuration between A and B types is also possible.

It has been well known that only the S_2-state exhibits the characteristic ESR signal, and this has been attributed to the presence of a Mn_2(III/IV) species in the S_2-state. However, we wish to propose a new interpretation on the S_2-state ESR signal on the basis of the following recent results,



(a) Ono *et al.* [43] observed that in the S_2-state a minor changes in the environment of the Mn, such as induced by replacement of Cl^- by SO_4^{2-} results in loss of the multiline ESR signal even though the oxidation state of the Mn cluster is proposed to be the same, and the readdition of Cl^- to such sample in the S_2-state results in formation of multiline ESR signal,

(b) Klein *et al.* [44] reported the ESR and X-ray absorption spectroscopy on the Mn oxygen-evolving center in cyanobacteria and found that illumination at 140 K results in the Mn oxidation ($S_1 \rightarrow S_2$), but no multiline or $g = 4$ ESR signal was observed,

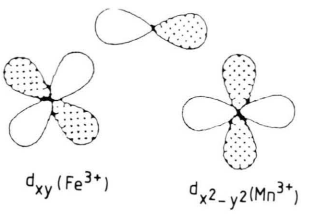
(c) both the multiline and $g = 4$ signals can be generated by continuous illumination at 200 K for the sample from spinach. The yield of both the signals varied with flash number with maxima after one and five flashes. These results strongly suggest that both signals are connected with the S_2-state. However, illumination at 140 K only generated the $g = 4$ signal, while subsequent thawing to 200 K results in an interconversion of this signal to the multiline signal [45].

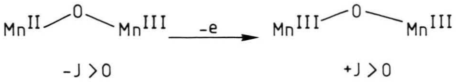
These facts are suggesting that the ESR signal observed for the S_2-state cannot be simply assigned to the oxidized species of X-pair in the S_1 to S_2 state transition, but rather to an another species formed in the course of this process.

Based on these facts and discussion, it seems reasonable to assume the oxidation state of the two dimers, 2.7 Å-pair and X-pair, to be as follows in the S_1-state;

2.7 Å-pair: Mn_2(III/III) with di-μ-oxo bridge
X-pair: Mn_2(II/III) with μ-oxo(or μ-OH) bridge.

The reasons will be developed. If the 2.7 Å-pair contains a Mn_2(III/IV) species, we cannot explain the fact that only the S_2-state exhibits a multiline ESR signal. Since the dimeric Mn(III) complexes where Mn-Mn distance is larger than 3.1 Å exhibit high magnetic moments (ferromagnetic interaction is operating, *cf.* Fig. 1), the results by Dismukes *et al.* can be reasonably explained on the assumption that X-pair shows antiferromagnetic interaction and has a large Mn-Mn distance (3.1–3.3 Å); roughly speaking $-J = 40\ cm^{-1}$ of the X-pair can explain the increase of magnetic moments ($\mu_{eff}^2 \sim 17$) observed in the S_1 to S_2 transition. Although no Mn_2(II/III) compound with μ-oxo (or μ-OH) bridge is known at present, we can expect that the moderate antiferromagnetic interaction may operate in these compounds, because strong antiferromagnetic interaction is observed for oxo-bridged Fe(III)-Mn(III) complex (the structure of this compound is isomorphus to the corresponding Mn_2(III/III) compound with (μ-oxo)bis(μ-acetato) core [34]) [46], which has an isoelectronic structure to a Mn_2(II/III) complex. The observed antiferromagnetism of binuclear Fe(III)-Mn(III) compound can be reasonably elucidated in terms of the "orbital model", taking the interaction pathway of $d_{xy}(Fe^{3+})$-oxygen-$d_{x^2-y^2}(Mn^{3+})$ into consideration [46] as depicted below; the most important point is that one unpaired electron lies in the d_{xy} orbital for Fe(III) and Mn(II) ions, and this interaction pathway is absent for the binuclear Mn_2(III/III) and Mn_2(III/IV) pairs with μ-oxo bridge. It is clear that only this model (illustrated below) can explain the increase of magnetic moment upon the oxidation of Mn ion. Then, there should be two Mn_2(III/III) pairs in the S_2-state, as described above. According to the recent works, the Mn_2(III/III) pairs of di-μ-oxo bridge is more oxidizable than other ones, such as that of (μ-oxo)bis(μ-acetato) core [34, 47]. If the interaction between two dimeric Mn_2(III/III) units with different redox potentials occurs, the following equilibrium may proceed,




$$\mathrm{Mn^{II}{-}O{-}Mn^{III}} \xrightarrow{-e} \mathrm{Mn^{III}{-}O{-}Mn^{III}}$$

$$\mathrm{Mn_2(III/III) + Mn_2(III/III)'} \rightleftharpoons \mathrm{Mn_2(III/IV) + Mn_2(III/II)'}$$

and thus partial formation of a Mn_2(III/IV) with di-μ-oxo bridge is expected. As the Mn_2(III/IV) species with di-μ-oxo bridge have been known to exhibit a "16-line ESR signal" [9, 10], ESR spectral properties observed for the Mn cluster in PS II can be reasonably elucidated in terms of the scheme described above.

Summary

(a) On the basis of EXAFS and magnetic susceptibility measurements, it was concluded that there are two dimeric Mn_2-unit in the oxygen-evolving center,

(b) one of them is a di-μ-oxo bridged dimer where two manganese ions are separated at 2.7 Å, and has Mn_2(III/III) oxidation state in both S_1 and S_2 states,

(c) a second binuclear unit which we will call as X-pair has Mn_2(II/III) oxidation state in S_1-state and is oxidized to Mn_2(III/III) state with μ-oxo bridge in the S_1 to S_2 state transition. This model can explain the results observed by Dismukes *et al.*,

(d) the multiline ESR signals observed for the S_2-state cannot be assigned to the oxidized X-pair, but rather to another species derived from the oxidized X-pair and the di-μ-oxo bridged pair of 2.7 Å separation. In this step the oxidation of the latter pair would occur and the formed Mn_2(III/IV) pair with di-μ-oxo bridge will explain the observed multiline ESR signal.

[1] G. W. Brudvig, Bioenerg. Biomembr. **19,** 91 (1987).

[2] G. T. Babcock, New Comprehensive Biochemistry (J. Amesz, ed.), Elsevier, North-Holland Press, Dordrecht 1987.

[3] G. C. Dismukes, Photochem. Photobiol. **43,** 99 (1986).

[4] G. Renger, Angew. Chem. Int. Ed. Engl. **26,** 643 (1987).

[5] B. Kok, B. Forbush, and M. McGroin, Photochem. Photobiol. **11,** 457 (1970).

[6] W. F. J. Vermaasm, G. Renger, and G. Gohnt, Biochim. Biophys. Acta **764,** 194 (1984).

[7] S. Styring and A. W. Rutherford, Biochem. **26,** 2401 (1987).

[8] G. C. Dismukes and Y. Siderer, FEBS Lett. **121,** 78 (1980).

[9] S. R. Cooper, G. C. Dismukes, M. P. Klein, and M. Calvin, J. Am. Chem. Soc. **100,** 7248 (1978).

[10] K. S. Hagen, W. H. Armstrong, and H. Hope, Inorg. Chem. **27,** 969 (1988).

[11] J. L. Casey and K. Saurer, Biochim. Biophys. Acta **767,** 21 (1984).

[12] J.-L. Zimmermann and A. W. Rutherford, Biochem. **25,** 4609 (1986).

[13] J. Cole, V. K. Yachandra, R. D. Guiles, A. E. McDermott, R. D. Britt, S. L. Dexheimer, K. Sauer, and M. P. Klein, Biochim. Biophys. Acta **890,** 395 (1987).

[14] M. W. Lynch, D. N. Hendrickson, B. J. Fitzgerald, and C. G. Pierpoint, J. Am. Chem. Soc. **106,** 2041 (1984).

[15] V. K. Yachandra, R. D. Guiles, A. E. McDermott, R. D. Britt, S. L. Dexheimer, K. Sauer, and M. P. Klein, Biochim. Biophys. Acta **850,** 324 (1986).

[16] V. K. Yachandra, R. D. Guiles, A. E. McDermott, R. D. Britt, S. L. Dexheimer, K. Sauer, and M. P. Klein, Biochem. **26,** 5974 (1987).

[17] M. Sivaraja, J. S. Philo, J. Lary, and G. C. Dismukes, J. Am. Chem. Soc. **111,** 3221 (1989).

[18] F. A. Cotton and R. A. Walton, "Multiple Bonds Between Metal Atoms", John Wiley & Sons, New York 1982.

[19] M. Kato, H. B. Jonassen, and J. C. Fanning, Chem. Rev. **64,** 99 (1964).

[20] P. A. M. Dirac, Proc. R. Soc. London, Ser, A, 1926, 112, 661; W. Heisenberg, Z. Phys. **38,** 41 (1926); J. H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities", Oxford University Press, London 1932.

[21] W. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, and W. E. Hatfield, Inorg. Chem. **15,** 2107 (1976).

[22] P. J. Hay, J. C. Thibeault, and R. Hoffmann, J. Am. Chem. Soc. **97,** 4884 (1975).

[23] O. Kahn, Angew. Chem. Int. Ed. Engl. **24,** 834 (1985).

[24] P. deLoth, P. Cassoux, J. P. Daudey, and J. P. Malrieu, J. Am. Chem. Soc. **103,** 4007 (1981).

[25] Y. Nishida, M. Takeuchi, K. Takahashi, and S. Kida, Chem. Lett. **1985,** 631; Y. Nishida and S. Kida, J. Chem. Soc. Dalton Trans. **1986,** 2633; Y. Nishida and S. Kida, Inorg. Chem. **27,** 447 (1988); Y. Nishida, T. Tokii, and Y. Mori, J. Chem. Soc. Chem. Commun. **1988,** 675; Y. Nishida, M. Masumoto, and Y. Morin, Z. Naturforsch. **44b,** 307 (1989).

[26] K. Wieghardt, U. Bossek, B. Nuber, J. Weiss, J. Bonvoisin, M. Corbella, S. E. Vitolis, and J. J. Girerd, J. Am. Chem. Soc. **110,** 7398 (1988).

[27] M. Stebler, A. Ludi, and H.-B. Burgi, Inorg. Chem. **25,** 4743 (1986).

[28] E. Libby, R. J. Webb, W. E. Streib, K. Folting, J. C. Huffman, D. N. Hendrickson, and G. Christou, Inorg. Chem. **28,** 4037 (1989).

[29] K. Wieghardt, U. Bossek, L. Zsolnai, G. Huttner, G. Blondon, J.-J. Girerd, and F. Babonneau, J. Chem. Soc. Chem. Commun. **1987,** 651.

[30] J. S. Bashkin, W. E. Streib, J. C. Huffman, H.-R. Chang, D. N. Hendrickson, and G. Christou, J. Am. Chem. Soc. **109,** 6502 (1987).

[31] M. Suzuki, H. Senda, Y. Kobayashi, H. Oshio, and A. Uehara, Chem. Lett. **1988,** 1763.

[32] P. M. Plaskin, R. C. Stoufer, M. Mathew, and G. J. Palenik, J. Am. Chem. Soc. **94,** 2121 (1972).

[33] M. A. Collins, D. J. Hodgson, K. Michelsen, and D. K. Towle, J. Chem. Soc. Chem. Commun. **1987,** 1659.

[34] K. Wieghartd, U. Bossek, D. Ventur, and J. Weiss, J. Chem. Soc. Chem. Commun. **1985,** 347.

[35] J. E. Sheats, R. S. Czernuszewicz, G. C. Dismukes, A. L. Rheingold, V. Petrouleas, J. Stubbe, W. H. Armstrong, R. H. Beer, and S. J. Lippard, J. Am. Chem. Soc. **109,** 1435 (1987).

[36] K. Wieghardt, U. Bossek, J. Bonvoisin, P. Beauvillain, J.-J. Girerd, B. Nuber, J. Weiss, and J. Heinze, Angew. Chem. Int. Ed. Engl. **25,** 1030 (1986).

[37] Y. Nishida, N. Oshino, and T. Tokii, Z. Naturforsch. **43b,** 472 (1988).

[38] K. Wieghardt, U. Bossek, and W. Gebert, Angew. Chem. Int. Ed. Engl. **22,** 328 (1983).

[39] K. S. Hagen, T. D. Westmoreland, M. J. Scott, and W. H. Armstrong, J. Am. Chem. Soc. **111,** 1907 (1989).

[40] R. K. Kulawiec, R. H. Crabtree, G. W. Brudvig, and G. K. Schlte, Inorg. Chem. **27,** 1311 (1988).

[41] J. B. Vincent, C. Christmas, H.-S. Chang, Q. Li, P. D. W. Boyd, J. C. Huffman, D. N. Hendrickson, and G. Chrstou, J. Am. Chem. Soc. **111,** 2086 (1989); K. S. Hagen, W. H. Armstrong, and M. M. Olmstaed, J. Am. Chem. Soc. **111,** 774 (1989).

[42] K. Takahashi, Y. Nishida, Y. Maeda, and S. Kida, J. Chem. Soc. Dalton Trans **1985,** 2375; S. J. Lippard, Angew. Chem., Int. Ed. Engl. **27,** 344 (1988).

[43] T. Ono, J.-L. Zimmermann, Y. Inoue, and A. W. Rutherford, Biochim. Biophys. Acta **851,** 193 (1986).

[44] A. E. McDermott, V. K. Yachandra, R. D. Guiles, J. L. Cole, S. L. Dexheimer, R. D. Britt, K. Sauer, and M. P. Klein, Biochem. **27,** 4021 (1988).

[45] J. C. de Paula, J. B. Innes, and G. W. Brudvig, Biochem. **24,** 8114 (1985).

[46] U. Bossek, T. Weyhermuller, K. Wieghardt, J. Bonvoisin, and J. J. Girerd, J. Chem. Soc. Chem. Commun. **1989,** 633.

[47] P. A. Goodson, J. Glerup, D. J. Hodgson, K. Michelsen, and E. Pedersen, Inorg. Chem. **29,** 503 (1990).