

Reprint

© VCH Verlagsgesellschaft mbH, Weinheim/Bergstr. 1988

Registered names, trademarks, etc. used in this journal, even without specific indication thereof, are not to be considered unprotected by law. Printed in Germany

International Edition in English

Structure, Magnetochemistry and Biological Relevance of $[Mn_4O_3Cl_4(OAc)_3(py)_3]$, a Complex with S=9/2 Ground State**

By Qiaoying Li, John B. Vincent, Eduardo Libby, Hsiu-Rong Chang, John C. Huffman, Peter D. W. Boyd, George Christou,* and David N. Hendrickson*

Two to four Mn ions serve as the active site for catalyzing the oxidation of two molecules of H₂O to give one molecule of O₂ during photosynthesis.^[1] Two research groups independently reported an EPR signal for the S₂ state of this site near photosystem II (PS II).^[2] This signal, comprising a $g \approx 2$ feature structured with 16-19 Mn hyperfine lines and a subsequently identified $g \approx 4$ feature, was shown to be consistent with a tetranuclear Mn₃^[1]Mn^{1V} site.^[3] The $g \approx 2$ feature has been assigned to a low-lying S = 1/2 excited state, and the $g \approx 4$ feature to either the S = 3/2 ground state of the same Mn₃^[1]Mn^{1V} site^[4] or to an S = 3/2 state of a different conformation of this site.^[5] These assignments are still matters of active discussion vis à vis detailed saturation, temperature dependence and sample history studies.

As part of our efforts to model this site, we recently reported the preparation of the first Mn¹¹¹₃Mn^{1V} complex 1.^[6]

 $(H_2Im)_2[Mn_4O_3Cl_6(HIm)(OAc)_3] \cdot 3/2 MeCN$ 1, HIm = imidazole, H_2Im^{\oplus} = imidazolium cation

[*] Prof. Dr. G. Christou, J. B. Vincent, E. Libby, Dr. J. C. Huffman Department of Chemistry and the Molecular Structure Center Indiana University Bloomington, IN 47405 (USA)
Prof. Dr. D. N. Hendrickson, Q. Li, H.-R. Chang, Dr. P. D. W. Boyd [*] School of Chemical Sciences, University of Illinois Urbana, IL 61801 (USA)

- [*] On sabbatical leave from the Chemistry Department of the University of Auckland, Auckland (New Zealand).
- [**] This work was supported by the U.S. National Institutes of Health (GM 39083 and HL 13652).

Angew. Chem. Int. Ed. Engl. 27 (1988) No. 12 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1988 0570-0833/88/1212-1731 \$ 02.50/0 1731

The low symmetry of 1 has prevented an accurate theoretical description of its electronic structure; however, we now report the synthesis of 2, a second complex of this type,

$[Mn_4O_3Cl_4(OAc)_3(py)_3] \cdot 3/2 MeCN 2$

which has crystallographically imposed C_3 symmetry, allowing an accurate quantum mechanical description of its electronic structure to be formulated. Of specific and considerable interest and potential relevance to the S₂-state EPR signal is the finding that complex **2** has an S=9/2 ground state with no low-lying excited states.

[Mn₃O(OAc)₆(py)₃](ClO₄) 3

A stirred brown solution of **3** (1.74 g, 2.0 mmol) in freshly distilled MeCN (80 mL) was treated dropwise with Me₃SiCl (0.60 mL, 4.7 mmol). Overnight storage of the deep red-brown solution gave black crystals of complex **2** which were collected by filtration, washed with MeCN, and dried; yield 15-20%.^[7] The complex has imposed C_3 symmetry (Fig. 1). As found for the anion of **1**, the



Fig. 1. Structure of complex **2** in the crystal. Selected bond distances [Å]: $Mn1 \cdots Mn2$, 2.815(2); $Mn1 \cdots Mn1'$, 3.272(2); Mn1-Cl3, 2.672(2); Mn1-Cl4, 2.237(2); Mn1-O5, 1.922(3); Mn1'-O5, 1.966(3); Mn1-O14, 2.146(3); Mn1-N6, 2.045(4); Mn2-O5, 1.865(3); Mn2-O12, 1.950(3). Primed and unprimed atoms are related by the threefold rotation axis.

 $[Mn_4(\mu_3-O)_3(\mu_3-Cl)]^{6\oplus}$ core is best considered as an Mn_4 pyramid with the Mn^{IV} ion Mn2 at the apex; the μ_3-Cl^{\ominus} ligand Cl3 bridges the basal plane, the $\mu_3-O^{2\ominus}$ ions bridge each remaining face. Alternatively, the core can be considered as a severely distorted Mn_4O_3Cl cubane. Three μ -OAc^{\ominus}, Cl^{\ominus} and py ligands complete the distorted octahedral geometry at each metal. Bridging Mn-Cl distances are appreciably longer than Mn-Cl terminal distances (2.627(2) vs. 2.237(2) Å), a point of potential relevance to the question of the possible presence of Cl^{\ominus} ligands in any of the S_n states of PSII as addressed by EXAFS studies.^[8]

The only available theoretical model^[4] to account for the magnetic exchange interactions in a cubic $Mn_3^{11}Mn^{1V}$ model complex for the S₂-state makes the assumption that an $Mn^{111}Mn^{1V}$ pair is strongly antiferromagnetically coupled to give an S = 1/2 state which is ferromagnetically coupled to the Mn^{III}Mn^{III} pair, the latter being itself weakly antiferromagnetically coupled. The C_3 symmetry of 2 eliminates the need to make these assumptions in interpreting the solid-state magnetochemistry of 2. As found^[6] for 1, the effective magnetic moment (μ_{eff}) per molecule of 2 increases gradually with decreasing temperature from 8.66 $\mu_{\rm B}$ at 301.9 K to a maximum of 9.27 $\mu_{\rm B}$ at 60.0 K, below which μ_{eff} decreases to 8.28 $\mu_{\rm B}$ at 5.0 K (Fig. 2a).



Fig. 2. a) Effective magnetic moment (μ_{eff}) per molecule as a function of the temperature *T* for $[Mn_4O_3Cl_4(OAc)_3(py)_3]\cdot 3/2 CH_3CN$ at 1 T. Data are shown as points and the solid line represents the least-squares fit to the theoretical susceptibility equation with $J_1(Mn^{1V}-Mn^{11I}) = -26.8 \text{ cm}^{-1}$, $J_2(Mn^{11}-Mn^{11I}) = +12.1 \text{ cm}^{-1}$ and g = 1.86. (The data were fit only down to 30 K because the decrease in the effective moment at lower temperatures is due to zero-field splitting. To include the effects of zero-field splitting, a full matrix diagonalization procedure needs to be employed where the matrix is 500×500 .) b) Plot of the molar magnetization (*M*) versus H/T for **2**, where *H* is the magnetic field in T and *T* is the temperature in K. Data were collected at three field strengths: \blacktriangle , 2.48 T: \bigoplus , 3.45 T: \square , 4.5 T. Three isofield lines are drawn for an S = 9/2 state with D = 0.32 cm⁻¹.

A Kambe vector-coupling model^[9] was derived for the C_3 -symmetric complex 2 by first coupling together the spin operators for the three Mn^{III} ions and then vectorially adding this to the spin operator for the Mn^{IV} ion. None of the assumptions of the previous model^[4] were needed.

Three parameters were employed to least-squares fit the susceptibility data for 2 to the equation resulting from the C_3 -symmetry vector-coupling model: J_1 for the three Mn^{IV}-Mn^{III} exchange interactions, J_2 for the Mn^{III}-Mn^{III} interactions, and an average g value. A systematic examination of the total parameter space (different sign combinations of J_1 and J_2 , initial parameter values, etc.) showed that three sets of parameters gave reasonable fits. In the format (J_1 , J_2 , g) these three sets are: (-376 cm^{-1} , -94.7 cm^{-1} , 2.14), ($+7.4 \text{ cm}^{-1}$, -3.6 cm^{-1} , 1.86) and (-26.8 cm^{-1} , $+12.1 \text{ cm}^{-1}$, 1.86), the estimated standard deviations in these parameters being $\pm 5\%$. Not only do these three fits deviate considerably from the view of the previous theoretical model, where J_1 is a large negative number and there is an S=3/2 ground state with a nearby

1732 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1988 0570-0833/88/1212-1732 \$ 02.50/0 Angew. Chem. Int. Ed. Engl. 27 (1988) No. 12

S = 1/2 excited state, the three fits are each quite different. The first gives an S = 7/2 ground state with an S = 9/2 excited state only 9 cm⁻¹ higher in energy. The second fit has an S = 9/2 ground state and an S = 7/2 excited state, separated by only 0.5 cm⁻¹ with seven other spin states lying within 50 cm⁻¹ of the ground state; whereas, the third fit has an S = 9/2 ground state with the closest excited state being S = 7/2 at 226 cm⁻¹ above the ground state. This third fit was used for the calculation of the unbroken curve in Figure 2a.

To our surprise, magnetization data for complex 2, collected over the temperature range 1.8 to 40 K at field values from 2.5 to 4.5 T, conclusively show an isolated S = 9/2 ground state (Fig. 2b). This is in agreement with the third set of parameters obtained from the susceptibility data. Additional support for the isolation of this S = 9/2 level is found in the fact that, although there are some changes and loss of resolution at elevated temperatures, the EPR spectrum of 2 (powder or glass) is readily seen at both liquid-helium and liquid-nitrogen temperatures. Such behavior would not be expected from the manifold of spin states found in the second fit.

It is likely that all the features in the glass EPR spectrum of 2 at $g \approx 2$, 6, and 9 (similar to those seen for 1,^[6]) are attributable to transitions between components of the S = 9/2 ground state, which, as a detailed analysis of the *M* versus H/T data (Fig. 2b) shows, experiences an axial zero-field splitting $(D\hat{S}_z^2)$ with D = 0.25 - 0.35 cm⁻¹. Whether the S₂ state of PS II contains a cluster similar to that of 2 is still unclear, but the described work does suggest that the possibility that the S₂-state EPR spectral features might also arise from components of a large-spin ground state should be seriously considered. Interestingly, we have just characterized^[10] a dinuclear Mn^{II}Mn^{III} complex which is also ferromagnetically coupled and has an S = 9/2 ground state (verified by *M* versus H/T data). The EPR spectrum for this Mn^{II}Mn^{III} complex is similar to those for 1 and 2.

> Received: June 28, 1988 [Z 2832 IE] German version: Angew. Chem. 100 (1988) 1799

- G. Renger, Angew. Chem. 99 (1987) 660; Angew. Chem. Int. Ed. Engl. 26 (1987) 643; G. C. Dismukes, Photochem. Photobiol. 43 (1986) 99; Govindjee, T. Kambara, W. Coleman, ibid. 42 (1985) 187; J. Amesz, Biochim. Biophys. Acta 726 (1983) 1.
- [2] G. C. Dismukes, Y. Siderer, Proc. Natl. Acad. Sci. USA 78 (1981) 274; O. Hansson, L. E. Andreasson, Biochim. Biophys. Acta 679 (1982) 261.
- [3] G. C. Dismukes, K. Ferris, P. Watnick, Photobiochem. Photobiophys. 3 (1982) 243.
- [4] J. C. de Paula, G. W. Brudvig, J. Am. Chem. Soc. 107 (1985) 2643; J.C. de Paula, W. F. Beck, G. W. Brudvig, *ibid.* 108 (1986) 4002; J. C. de Paula, J. B. Innes, G. W. Brudvig, *Biochemistry* 24 (1985) 8114.
- [5] O. Hansson, R. Aasa, T. Vanngard, Biophys. J. 51 (1987) 825; J. L. Zimmerman, A. W. Rutherford, Biochemistry 25 (1986) 4609.
- [6] J. S. Bashkin, H.-R. Chang, W. E. Streib, J. C. Huffman, D. N. Hendrickson, G. Christou, J. Am. Chem. Soc. 109 (1987) 6502.
- [7] Correct elemental analysis for C₂₄H_{28.5}N_{4.5}O₉Cl₄Mn₄; X-ray structure data: rhombohedral, space group R3, T=-155°C, a=b=c=13.031(4) Å, α=β=γ=74.81(2)°, Z=2, data collected 6° ≤ 2θ ≤ 45°, 1458 unique reflections with F>3.00σ(F), R=0.0371, R_w=0.0417. All non-solvent hydrogen atoms were located in a difference Fourier and included in the final refinement cycles with isotropic thermal parameters. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (UK), on quoting the complete journal citation.
- [8] V. K. Yachandra, R. D. Guiles, A. McDermott, R. D. Britt, S. L. Dexheimer, K. Sauer, M. P. Klein, Biochim. Biophys. Acta 850 (1986) 324.
- [9] K. Kambe, J. Phys. Soc. Jpn. 5 (1950) 48.
 [10] J. S. Bashkin, A. R. Schake, J. B. Vincent, H.-R. Chang, Q. Li, J. C. Huffman, G. Christou, D. N. Hendrickson, J. Chem. Soc. Chem. Commun. 1988, 700.

Angew. Chem. Int. Ed. Engl. 27 (1988) No. 12 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1988 0570-0833/88/1212-1733 \$ 02,50/0 1733