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## Structural Characterization of the Manganese(IV) Schiff-Base Complex $\text{Mn}^{\text{IV}}(\text{5-Cl-SALAH})_2$

BY XINHUA LI, MYOUNG SOO LAH AND VINCENT L. PECORARO\*

*Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, USA*

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**Abstract.** Bis[3-(5-chlorosalicylideneamino)propanolato-*O,N,O'*]manganese(IV) methanol solvate,  $[\text{Mn}(\text{C}_{10}\text{H}_{10}\text{ClNO}_2)_2]\cdot\text{CH}_3\text{OH}$ ,  $M_r = 510.3$ , monoclinic,  $P2_1/c$ ,  $a = 11.949$  (2),  $b = 7.530$  (2),  $c = 25.777$  (6) Å,  $\beta = 105.75$  (2)°,  $V = 2232.4$  (8) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.518$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.7107$  Å,  $\mu = 7.98$  cm<sup>-1</sup>,  $F(000) = 1502$ ,  $T = 300$  K,  $R = 0.0343$ ,  $wR = 0.032$  for 2113 unique reflections with  $(I) > 3\sigma(I)$ . The title complex  $\text{Mn}^{\text{IV}}(\text{5-Cl-SALAH})_2$  [5-Cl-SALAH = 3-(5-chlorosalicylideneamino)propanolato] displays a regular octahedral geometry. The 5-Cl-SALAH ligand is tridentate, forming a meridional chelate with one phenolato oxygen ( $\text{Mn}-\text{O}_{\text{avg}} = 1.90$  Å), one alkoxide oxygen ( $\text{Mn}-\text{O}_{\text{avg}} = 1.85$  Å) and one imine nitrogen ( $\text{Mn}-\text{N}_{\text{avg}} = 2.02$  Å) coordinated to the metal. Important angles described by the six atoms bound to manganese are all very close to either 180 or 90° except the N—Mn—N angle which is 174.7°. Previous studies have shown that  $\text{Mn}^{\text{IV}}(\text{5-Cl-SALAH})_2$  displays a rhombic EPR spectrum with well-resolved <sup>55</sup>Mn hyperfine structure on  $g_x$ ,  $g_y$ , and  $g_z$ . In contrast,  $\text{Mn}(\text{SALADHP})_2$  [SALADHP = 2-methyl-2-(salicylideneamino)-1,3-propanediolato] shows a broad, ill-defined signal at  $g = 5.15$  and a weak  $g = 2$  component. The different spectral forms result from the extent of distortion of the  $\text{Mn}^{\text{IV}}$  octahedron. The reported structure is of potential importance to the understanding of the photosynthetic water-oxidizing system.

**Introduction.** Elucidation of the structure of the metalcenter of the photosynthetic oxygen-evolving complex (OEC) has garnered considerable interest in recent years. The  $\text{Mn}^{\text{IV}}$  oxidation level has been invoked as an intermediate in nearly every model that has been proposed for this enzymic reaction (Pecoraro, 1988; Babcock, 1987). The EPR spectral features in the  $S_2$  oxidation level of the OEC have fueled considerable debate regarding the core structure and metal oxidation states of the manganese (de Paula, Beck & Brudvig, 1986; Hansson, Aasa & Vanngard, 1987). Both a  $g = 2$  multiline (Dismukes & Siderer, 1980) and a  $g = 4.1$  derivative signal have been observed using the spinach enzyme (Casey & Sauer, 1984). A tetranuclear model that invoked a conformational change for the origin of the two signals was initially proposed (de Paula, Beck & Brudvig, 1986); however, a new interpretation assigns the  $g = 2$  multiline signal to a mixed-valence dimer and the  $g = 4$  signal to a mononuclear  $\text{Mn}^{\text{IV}}$  (Hansson, Aasa & Vanngard, 1987). A mononuclear/trinuclear formulation has also been put forward (Pecoraro, 1988). Recently, it was noted that the  $g = 4$  signal could not be generated from photosynthetic membranes of the cyanobacterium *Synechococcus* (McDermott, Yachandra, Guiles, Cole, Dexheimer, Britt, Sauer & Klein, 1988). These authors suggested that the different behavior of the spinach and *Synechococcus* enzymes may be due to changes in the zero-field splitting parameters of  $\text{Mn}^{\text{IV}}$ . Unfortunately, there are very few structurally characterized  $\text{Mn}^{\text{IV}}$  complexes with reported EPR spectra.

\* To whom correspondence should be addressed.

We have shown previously that the Mn<sup>IV</sup>[1,3-dihydroxy-2-methyl-2-(salicylideneamino)propanato]<sub>2</sub> complex has a broad, ill-defined EPR signal while Mn<sup>IV</sup>[1-hydroxy-3-(salicylideneamino)propanato]<sub>2</sub> gave a well resolved <sup>55</sup>Mn hyperfine signal (Kessissoglou, Li, Butler & Pecoraro, 1987). Herein, we report the structure of Mn(5-Cl-SALAH<sub>2</sub>), which also exhibits a well resolved <sup>55</sup>Mn hyperfine signal, and compare its structure to Mn<sup>IV</sup>-(SALADHP)<sub>2</sub>. Through this study we hope to define structural constraints that may be important for a full understanding of the photosynthetic water-oxidizing system.

**Experimental.** All manipulations were carried out using standard inert-atmosphere techniques and distilled solvents. The Schiff base 3-(5-chlorosalicylideneamino)propanol was formed by the condensation of 5-chlorosalicylaldehyde (0.02 mol) with 3-amino-1-propanol (0.02 mol) in methanol. The title complex was prepared *via* an MnCl<sub>2</sub>.4H<sub>2</sub>O (0.01 mol) reaction with two equivalents of 5-Cl-SALAH<sub>2</sub> and two equivalents of NaOH (0.02 mol) in methanol at refluxing temperature. Aerial oxidation of the manganese yielded a purple solid which gave crystals of Mn(5-Cl-SALAH<sub>2</sub>) when recrystallized from CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub>. Dark-red block (0.26 × 0.20 × 0.32 mm); Syntex P<sub>2</sub> diffractometer; least-squares refinement of 15 reflections in the range 15 < 2θ < 22° for cell constant determination; systematic absences: 0k0, k = 2n + 1; h0l, l = 2n + 1; 2θ<sub>max</sub> = 40°; h: 0 to 12, k: 0 to 8, l: -26 to 26; no absorption correction; less than 5% random variation in three standard reflections (527, 332, 2.0.10) measured every 50 reflections; no significant crystal decay; scan speed variable based on intensity, 2.5–12° min<sup>-1</sup>; 2934 data collected; θ–2θ scans; 2113 unique reflections with (I) > 3σ(I); background/scan time ratio 0.8; data reduced using SHELX (Sheldrick, 1976); structure by direct methods (SHELXS86; Sheldrick, 1986); refined with anisotropic thermal parameters for all non-H atoms. H-atom positions were calculated and included in F<sub>c</sub>, but not refined, with fixed U values of 0.05; function minimized Σw(|F<sub>o</sub>| – |F<sub>c</sub>|)<sup>2</sup> with w = 1/[σ<sup>2</sup>(F) + 0.0001F<sup>2</sup>]; final R = 0.034, wR = 0.032. Maximum shift/e.s.d. was < 0.33. Final difference Fourier map contained no peaks < –0.40 or > 0.32 e Å<sup>-3</sup>. Goodness of fit was 1.22. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The nearly octahedral coordination of the Mn<sup>IV</sup> ion in the title complex is illustrated in Fig. 1. The fractional atomic coordinates and equivalent isotropic temperature factors for the non-H atoms

are listed in Table 1.\* Important bond lengths and angles have been summarized in Table 2. The 5-Cl-SALAH<sub>2</sub> ligands are tridentate and form meridional bis(chelates) with one phenolate oxygen (O1, O3), one deprotonated alkoxide oxygen (O2, O4), and one imine N atom (N1, N2) coordinated to manganese. Mn–O<sub>alk</sub> (avg. = 1.848 Å) are shorter than Mn–O<sub>phe</sub> (avg. = 1.899 Å), and Mn–N (avg. = 2.017 Å) are longer than Mn–O<sub>phe</sub>. These distances are in the right range for Mn<sup>IV</sup>–O and Mn<sup>IV</sup>–N bonds. Mn(5-Cl-SALAH<sub>2</sub>) (1) is nearly isostructural with Mn(SALADHP)<sub>2</sub> (2) (Kessissoglou, Li, Butler & Pecoraro, 1987). The lengths for Mn–N and Mn–O bonds of both structures are comparable. The only marked deviation is in Mn–O4 [1.854 vs 1.923 Å in (1) and (2), respectively]. The angles associated with the Mn<sup>IV</sup> coordination sphere in (1) are much closer to 90 or 180° than in (2). Marked deviations are again associated with the Mn–O4 bond in (2). For example, the bond-angle differences for (1) and (2) are 8 to 10° for O3–Mn1–O4 [179.5° for (1), 171.6° for (2)] and O4–Mn1–N2 [92.0° for (1), 82.9° for (2)]. We believe that the more highly symmetric octahedron observed in (1) probably results from the additional methylene group in SALAH<sub>2</sub>, which allows for the formation of a six-membered chelate ring rather than the five-membered ring formed by SALADHP. These distances are in good agreement with the corresponding bonds in the complex bis(salicylato)-(bipyridine)manganese(IV), which has been studied recently (Pavacic, Huffman & Christou, 1986).

The additional methylene group, which led to a more highly symmetric structure for (1), has direct implications for the chemistry of the molecule. Although still strongly stabilized as Mn<sup>IV</sup> due to the alkoxide ligation, the Mn<sup>IV</sup> to Mn<sup>III</sup> reduction for (1)

\* Tables of anisotropic thermal parameters, H-atom parameters, distances and angles, and observed and calculated structure amplitudes, and a figure giving the complete numbering scheme for the molecules have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52021 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

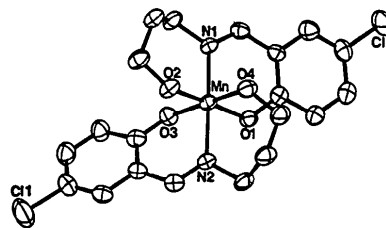


Fig. 1. ORTEP diagram (Johnson, 1965) of Mn(5-Cl-SALAH<sub>2</sub>)<sub>2</sub> with thermal ellipsoids at 30% probability.

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Mn1	0.7679	0.0990 (1)	0.2924	0.029
Cl1	0.4178 (1)	0.2060 (2)	0.4769 (1)	0.078
Cl2	0.8693 (1)	0.2838 (2)	0.0387 (1)	0.091
O1	0.6927 (2)	0.2777 (3)	0.3221 (1)	0.035
O2	0.8455 (2)	-0.0703 (3)	0.2639 (1)	0.037
O3	0.6791 (2)	0.1680 (3)	0.2222 (1)	0.033
O4	0.8532 (2)	0.0312 (3)	0.3609 (1)	0.038
N1	0.6367 (2)	-0.0693 (4)	0.2934 (1)	0.029
N2	0.8872 (2)	0.2820 (4)	0.2874 (1)	0.030
C1	0.6363 (3)	0.2509 (5)	0.3591 (2)	0.030
C2	0.6296 (3)	0.3927 (6)	0.3938 (1)	0.036
C3	0.5664 (3)	0.3760 (6)	0.4307 (2)	0.040
C4	0.5056 (3)	0.2190 (6)	0.4328 (2)	0.043
C5	0.5110 (3)	0.0795 (6)	0.3999 (2)	0.043
C6	0.5779 (3)	0.0925 (5)	0.3630 (1)	0.032
C7	0.5734 (3)	-0.0526 (5)	0.3264 (1)	0.034
C8	0.6058 (3)	-0.2120 (5)	0.2532 (2)	0.043
C9	0.7104 (3)	-0.3179 (5)	0.2494 (2)	0.042
C10	0.7944 (3)	-0.2086 (6)	0.2285 (2)	0.044
C11	0.7261 (3)	0.1928 (5)	0.1818 (2)	0.035
C12	0.6610 (3)	0.1524 (6)	0.1294 (2)	0.042
C13	0.7056 (4)	0.1807 (6)	0.0865 (2)	0.049
C14	0.8177 (4)	0.2507 (6)	0.0949 (2)	0.048
C15	0.8835 (3)	0.2945 (5)	0.1455 (2)	0.039
C16	0.8400 (3)	0.2639 (5)	0.1902 (1)	0.031
C17	0.9060 (3)	0.3237 (5)	0.2422 (2)	0.032
C18	0.9529 (3)	0.3792 (6)	0.3364 (2)	0.039
C19	1.0056 (3)	0.2557 (6)	0.3829 (2)	0.040
C20	0.9139 (3)	0.1525 (5)	0.4010 (2)	0.041
O5	0.8107 (4)	-0.2830 (5)	0.4046 (2)	0.102
C21	0.8219 (5)	-0.2589 (9)	0.4587 (2)	0.102

occurs at a potential about 200 mV more positive than for (2). In addition, the cyclic voltammogram is more electrochemically reversible. These observations suggest that the SALAHP ligand can more easily accommodate the Mn<sup>III</sup> oxidation level which almost invariably shows a 0.2 Å axial elongation (Mikuriya, Torihara, Okawa & Kida, 1981). The already strained Mn1—O4 ligation in Mn (SALADHP)<sub>2</sub> can not tolerate an additional 0.2 Å elongation and, therefore, the Mn<sup>III</sup> oxidation level is destabilized by nearly four orders of magnitude.

The different EPR spectral behavior is most likely due to the deviations from octahedral symmetry. The EPR spectrum of (1) shows well-defined <sup>55</sup>Mn nuclear hyperfine structure on the resonances at  $g_{eff} = 1.96, 4.38$  and  $5.91$ . The distortions of the manganese polyhedron in (2) lead to a broad, featureless spectrum with a turnover point at  $g_{eff} = 5.15$ . From these observations, we suggest that if *Synechococcus* contains a mononuclear Mn<sup>IV</sup> it is most likely in a

Table 2. Selected bond distances (Å) and angles (°)

Mn1—O1	1.892 (2)	Mn1—O2	1.842 (2)
Mn1—O3	1.905 (2)	Mn1—O4	1.854 (2)
Mn1—N1	2.022 (3)	Mn1—N2	2.012 (3)
O1—Mn1—O2	178.1 (1)	O1—Mn1—O3	89.3 (1)
O2—Mn1—O3	91.2 (1)	O1—Mn1—O4	90.5 (1)
O2—Mn1—O4	89.0 (1)	O3—Mn1—O4	179.5 (1)
O1—Mn1—N1	89.1 (1)	O2—Mn1—N1	92.7 (1)
O3—Mn1—N1	87.1 (1)	O4—Mn1—N1	92.4 (1)
O1—Mn1—N2	87.8 (1)	O2—Mn1—N2	90.4 (1)
O3—Mn1—N2	88.5 (1)	O4—Mn1—N2	92.0 (1)
N1—Mn1—N2	174.7 (1)		

more highly distorted environment than (2). In contrast, the mononuclear Mn<sup>IV</sup> of higher plant photosynthesis would have an environment somewhere between (1) and (2), or possibly a trigonal distortion.

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