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$[L_2Mn_2(\mu\text{-}O)_2(\mu\text{-}O_2)](ClO_4)_2$: The First Binuclear ($\mu$-Peroxo)dimanganese(IV) Complex (L = 1,4,7-Trimethyl-1,4,7-triazacyclononane). A Model for the $S_4 \rightarrow S_0$ Transformation in the Oxygen-Evolving Complex in Photosynthesis

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Light-driven oxidation of water to molecular oxygen in photosystem II (PS II) has been shown to occur at an active site comprising four manganese ions.[2] There are five kinetically resolved intermediates in the catalytic cycle which have been designated S_0 to S_4.[3] S_0 represents the most reduced and S_4 the most oxidized level. The transformation $S_4 \rightarrow S_0$ involves the release of O_2 and regeneration of the S_0 level. Virtually all proposed mechanistic schemes invoke a peroxodimanganese complex as precursor to the release of O_2.[4] It is therefore surprising that only two low-molecular-weight peroxo complexes of manganese(III) have been structurally characterized: monomeric $[K(crypt)][Mn(TPP)O_2]$[5] and trinuclear $[Mn_3(dien)_3(OAc)_2(\mu\text{-}O)(\mu\text{-}O_2)]I_3{\cdot}H_2O{\cdot}0.33CH_3OH$.[6] In contrast, a large number of bi-, tri-, and tetranuclear complexes modeling the *spatial* arrangement of the Mn ions in PS II have in recent years been investigated.[7] Here we report the synthesis and X-ray structure of the first (μ-peroxo)dimanganese(IV) complex, $[L_2Mn_2(\mu\text{-}O)_2(\mu\text{-}O_2)](ClO_4)_2$ (**1**) (L = 1,4,7-trimethyl-1,4,7-triazacyclononane), as a model for part of the $S_4 \rightarrow S_0$ transformation in PS II.

When a methanolic (50 mL) solution of $Mn(ClO_4)_2{\cdot}6H_2O$ (0.50 g), 1,4,7-trimethyl-1,4,7-triazacyclononane (0.5 g), and sodium methanolate (0.20 g) was allowed to react with air at -5 °C, a deep brown solution was obtained, from which, after addition of $NaClO_4$ (2 g) and standing in a refrigerator at 0 °C for 3 days, small brown needles of **1** crystallized (yield: 0.2 g).[8] From susceptibility measurements in the temperature range 81-293 K on a powdered sample of **1**, using the Faraday method, temperature-dependent magnetic moments of 1.2 μ_B at 81 K and 2.5 μ_B at 293 K per dimeric unit were calculated, which indicate intramolecular antiferromagnetic coupling between the two Mn(IV) ions (d^3).

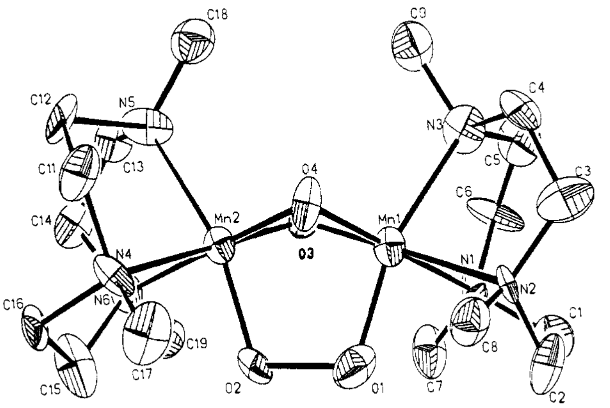

Figure 1. View of the dication of **1** with atom-labeling scheme. Selected bond distances (Å) and angles (deg): Mn(1)–O(1), 1.83 (2); Mn(1)–O(3), 1.81 (2); Mn(1)–O(4), 1.82 (2); Mn(2)–O(2), 1.83 (2); Mn(2)–O(3), 1.81 (2); Mn(2)–O(4), 1.81 (2); O(1)–O(2), 1.46 (3); O(3)- - -O(4), 2.41 (3); O(3)–Mn(1)–O(4), 83.1 (7); O(3)–Mn(2)–O(4), 83.5 (7); Mn(1)–O(3)–Mn(2), 88.8 (6); Mn(1)–O(4)–Mn(2), 88.4 (5); Mn(2)–O(2)–O(1), 106.9 (12); O(2)–O(1)–Mn(1), 106.9 (13); O(4)–Mn(2)–O(2), 92.4 (7); O(3)–Mn(2)–O(2), 93.4 (7); O(4)–Mn(1)–O(1), 91.2 (8); O(3)–Mn(1)–O(1), 94.6 (8).

Figure 1 shows the structure of the dication in a crystal of **1**.[10] Two Mn^{IV} ions are connected by two μ_2-oxo groups and an O,O′-coordinated peroxo bridge; two triamine capping ligands complete the distorted octahedral environment about each metal center.[11] The average $Mn\text{–}O_{oxo}$ bond length is 1.81 (2) Å, in good agreement with many other bis(μ-oxo)dimanganese(IV) units.[7,9] The average $Mn\text{–}O_{peroxo}$ distance of 1.83 (2) Å is also quite short. The O–O distance of 1.46 (3) Å is typical for bridging peroxo groups.[12] Interestingly, the four-membered Mn_2O_2 ring is puckered, contrasting in this respect with many analogous Mn^{IV} complexes that contain planar Mn_2O_2 rings. The average Mn–N bond distance of 2.11 Å is in excellent agreement with those of $[L_2Mn^{IV}{}_2(\mu\text{-}O)_3](PF_6)_2{\cdot}H_2O$.[13] The Mn···Mn distance in **1** is 2.531 (7) Å.

Solutions of **1** in CH_3CN are stable at ambient temperature for many hours. In contrast, **1** decomposes rapidly in aqueous solution under anaerobic conditions (Ar) at 20 °C, with the release of molecular oxygen as was established by GC analysis, mass spectrometry, and measurements with an O_2-sensitive electrode.[14] During this reaction the pH increases. Quantitative measurement of the O_2 released in buffered solutions[15] in the absence of coordinating ligands shows that 75% of the bound peroxide in **1** is released. The presence of 50% $[L_2Mn^{IV}{}_2(\mu\text{-}O)_3]^{2+}$ based on **1** in the product mixture was determined spectrophotometrically. The product distribution was found to be independent of pH in the range 3-8. Mechanistically our results indicate a sequence of events where the initial intramolecular 2e⁻ oxidation of coordinated $O_2{}^{2-}$ occurs with concomitant reduction of Mn^{IV} yielding a binuclear manganese(III) intermediate. Disproportionation of this intermediate then forms the stable $[LMn^{IV}(\mu\text{-}O)_3Mn^{IV}L]^{2+}$ species and a manganese(II) dimer, which probably dissociates to a

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[8] Anal. Calcd for **1** ($C_{18}H_{42}Cl_2Mn_2N_6O_{12}$): C, 30.22; H, 5.92; N, 11.75; Cl, 9.91; Mn, 15.36. Found: C, 29.9; H, 5.8; N, 11.5; Cl, 10.2; Mn, 15.6. UV–vis (CH_3CN; 20 °C): λ_{max} (nm) (ϵ, L mol^{-1} cm^{-1}) 282 (1.9×10^4), 420 (sh), 500 (sh), 580 (sh), 700 (690), 769 (590).

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[11] The dication in **1** does not possess crystallographically imposed symmetry. The coordination geometry at both Mn ions is identical within experimental error. This together with the O–O distance of 1.46 Å rules out the formulation of **1** as a mixed-valence $Mn^{III}Mn^{IV}$ dimer with a coordinated superoxide $O_2{}^-$ ligand.

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[14] Membrane-covered amperometric Clark electrode (WTW EO 90).

[15] Solutions used: (a) H_2O, 0.05 M 2,4,6-trimethylpyridine, 0.025 M CH_3SO_3H (pH 7.2); (b) 0.01 M CH_3SO_3H (pH 2.0); (c) 0.001 M CH_3SO_3H (pH 3). The concentration of **1** was varied between 1.0×10^{-4} and 0.4×10^{-4} M, respectively. In all cases the buffer solutions were purged with argon before solid samples of **1** were added.

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monomeric species $[LMn(OH_2)_3]^{2+}$. Rapid oxidation of this monomer to a LMn^{III} species can then be achieved by the O_2 present in solution. When the same reaction was carried out in a solution containing chloride ions (0.5 M) at pH 3, under otherwise identical conditions, 100% O_2 was released. The spectrum of the resulting solution is very similar to that of $LMn^{III}Cl_3$.[13] Thus the above disproportionation reaction does not occur. This result may have interesting implications on the functional role of Cl^- in PS II.

Presently we are studying the mechanism of formation and decomposition and the reactivity of **1** in detail.

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Supplementary Material Available: Tables of complete crystallographic data, atom coordinates, calculated positions of H atoms, and anisotropic thermal parameters for $[L_2Mn_2(\mu\text{-}O)_2(\mu\text{-}O_2)](ClO_4)_2$ (6 pages); listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

Diazotization of 1-Aminocyclopropanecarboxylic Acid. Solution Chemistry of Oxaspiropentanone

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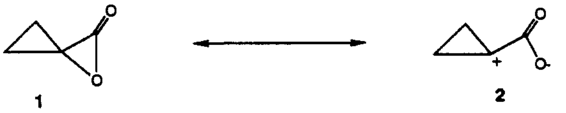
The retention of stereochemistry in the nitrosative deamination of α-amino acids is explained by the intermediate formation of α-lactones.[2] Neighboring-group participation occurs with inversion of stereochemistry, followed by nucleophilic α-alkyl C–O bond cleavage. The strain of α-lactones makes them intrinsically reactive; they are generally unstable, undergoing polymerization at temperatures above −100 °C in a process explainable via zwitterionic no-bond resonance forms.[3] Theoretical studies suggest, though, that such zwitterions are chimeric.[4]

The reactivity of α-lactones is influenced by steric and by electronic factors. The behavior of tertiary α-amino acids under diazotization conditions is consistent with an increased zwitterionic character of the α-lactone; some racemization and carbonium ion rearrangements are observed.[5] On the other hand, di-*tert*-butylacetolactone persists at −60 °C,[6] bis(trifluoromethyl)acetolactone is stable in solution or the gas phase,[7] and a hindered perfluoroacetolactone is isolable.[8] It may be considered that oxaspiropentanone (**1**) would be stabilized by decreased contribution of the no-bond resonance form **2** due to the high energy of a cyclopropyl carbocation (eq 1). Alternatively, the combined strain of two three-membered rings might confer decreased stability. A number of α-lactones, including **1**, have been accessible for study by matrix isolation at 77 K,[9] but no solution chemistry of **1** is known. This communication reports the first evidence for the existence of **1** in solution and its participation in synthetic transformations.

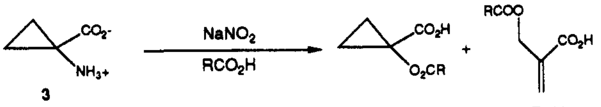
Table I

[ACC], mM	[KBr], mM	**4b**:**6**	**5b**:**7**	(**4b** + **6**):(**5b** + **7**)
180	0 (0 equiv)	100:0	100:0	86:14
135	135 (1 equiv)	93:7	>99:1	86:14
145	435 (3 equiv)	92:8	>99:1	86:14
125	635 (5 equiv)	89:11	83:17	86:14
140	995 (7 equiv)	71:29	71:29	87:13
260	sat (10 equiv)	58:42	67:33	87:13

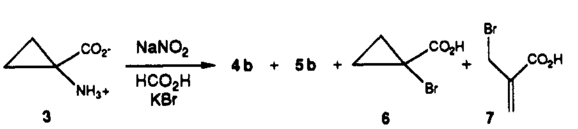


1 **2** (1)

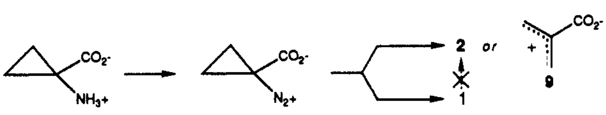
Standard conditions for diazotization[10] (1 equiv of sodium nitrite, glacial acetic acid) were applied to 1-aminocyclopropanecarboxylic acid (ACC, eq 2). The major product, isolated in 60% yield, is 1-acetoxycyclopropanecarboxylic acid (**4a**).[11] (Hydroxymethyl)acrylic acid derivative **5a** is obtained as 3% of the total product. Increasing the solvent polarity (anhydrous formic acid) leads to a greater proportion of ring-opening product **5b** (13%). The hypothesis that the α-lactone is the precursor to both **5** (via **2**) and **4** was tested by a competition study between formate and bromide as nucleophiles (eq 3). As shown herein, it is possible to obtain substitution products with other nucleophiles in solvents of low nucleophilicity. The data in Table I show both ring-opening and substitution products incorporating both nucleophiles. As expected, the proportion of bromides increases with increasing bromide ion concentration, but the proportion of ring-opening products remains constant. Therefore, α-lactone **1** cannot be the common intermediate, and diazonium ion **8** is suggested. Partitioning between the two pathways must be an irreversible, unimolecular, and solvent-dependent process. There must be an intermediate between **8** and substitution products which does not ring-open. Likewise, **2** may not be involved in substitution. These requirements are met by eq 4. It is not possible on the basis of these data to determine whether loss of nitrogen leads to **2** or directly to the allyl cation **9**.



3 **4a** R=Me **4b** R=H **5a** R=Me **5b** R=H (2)



3 **6** **7** (3)



3 **8** (4)

Stereochemical studies also support oxaspiropentanone **1** as the intermediate in the substitution reaction. Both (1*R**,2*S**)- and (1*R**,2*R**)-2-ethyl-1-aminocyclopropanecarboxylic acid are available from a previous study.[12] When treated under the above

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[11] After acetylation of the crude reaction mixture. Omitting this step reduces the yield to 42%, presumably because the extremely water soluble 1-hydroxycyclopropanecarboxylic acid is also produced by competitive nucleophilic trapping with water. Including sodium acetate (10 equiv) in the diazotization reaction similarly increases the yield to 50%.

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