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[6] a) X-ray structure analysis of $[Ru(bpy)_2(H_2saltsc)]ClO_4 \cdot 1/2\,C_6H_6 \cdot 1/2\,CH_2Cl_2$: $C_{31.50}H_{27}Cl_2N_7O_5RuS$, $M_r = 787.63$, monoclinic, space group $P2_1/c$, $a = 9.169(1)$, $b = 16.396(2)$, $c = 24.634(3)$ Å, $\beta = 99.075(8)^\circ$, $V = 3657.0(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.431$ Mg m^{-3}; crystal dimensions $0.50 \times 0.30 \times 0.02$ mm. Data ($2\theta_{max} = 51.1^\circ$) were collected at 293(2) K on a Rigaku RAXIS-IIC imaging plate with graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu = 0.597$ mm^{-1}, transmission factors 0.755–1.148. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were included but not refined. $R1 = 0.1267$ for 3296 observed reflections ($I > 2\sigma(I)$) and 418 parameters; $wR2 = 0.3507$ for 4634 unique reflections. Programs used: SHELXS-97 (structure solution) and SHELXL-97 (structure refinement). b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-156075 and -156076. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[7] X-ray structure analysis of $[\{Ru(bpy)_2(saltsc)\}_4Ni_4](ClO_4)_4 \cdot 4\,C_6H_6 \cdot 2\,MeCN$: $C_{140}H_{118}Cl_4N_{30}Ni_4O_{20}Ru_4S_4$, $M_r = 3449.80$, monoclinic, space group $P2/n$, $a = 18.386(3)$, $b = 12.268(2)$, $c = 36.398(6)$ Å, $\beta = 104.219(3)^\circ$, $V = 7959(2)$ Å^3, $Z = 2$; crystal dimensions $0.60 \times 0.47 \times 0.28$ mm, intensities ($2\theta_{max} = 56.2^\circ$) were collected at 293(2) K on a Bruker SMART 1000 CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu = 1.020$ mm^{-1}; absorption corrections with the SADABS program yielded relative transmission factors of 0.8075–1. $R1 = 0.0795$ for 10301 observed reflections ($I > 2\sigma(I)$) and 932 parameters; $wR2 = 0.2672$ for 19288 reflections.[6b]

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Selective Photoproduction of O_2 from the Mn_4O_4 Cubane Core: A Structural and Functional Model for the Photosynthetic Water-Oxidizing Complex**

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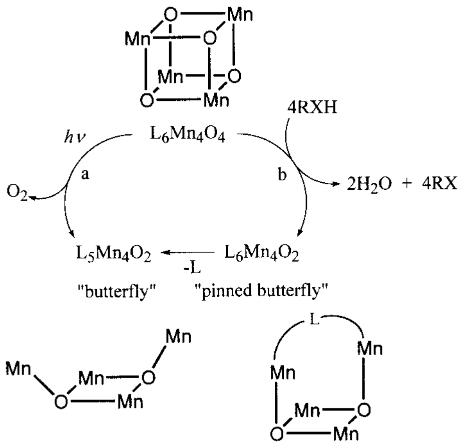
Dedicated to Dr. Peter Gabriel

Both the announcement last year by the German Federal Government to eliminate the use of nuclear power generators by 2021[1] and the recent shortage of electric power in California USA place renewed emphasis on development of socially acceptable energy sources such as solar[2] and fuel cells.[3] The latter cells rely on energy generated by the combination of H_2 (or hydrocarbons) with O_2. Both of these molecules are expected to be produced by solar-based water-splitting catalysts ($H_2O \rightarrow \tfrac{1}{2}O_2 + H_2$), hence, the efforts to understand Nature's photosynthetic process of O_2 generation by water oxidation in plants,[4] and to functionally mimic the catalytic center,[5, 6] take on a pressing schedule. Key advances have occurred recently on both fronts with the first X-ray crystal structure at 3.8 Å resolution of the water-oxidizing complex (WOC) and its associated photochemical reaction center (photosystem II) from a cyanobacterium[7] and the first report of intramolecular O_2 photoproduction from the bridging oxygen atoms of a manganese–oxo cluster of cubane-type geometry, $L_6Mn_4O_4$ (**1**; L = diphenylphosphinate; $Ph_2PO_2^-$)



Scheme 1. Reactions of $L_6Mn_4O_4$ cubane complexes **1** and **1′**: a) UV photochemical reaction in the gas phase and b) reductive dehydration reaction in solution. RXH = organoammine, phenol, etc. Bridging phosphinates omitted for clarity.

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(Scheme 1 path a).[8] O_2 release may proceed via a bridging peroxo transition state. This core type appears to be structurally similar to the WOC in its highest oxidation state.[9, 10] Complex **1** can also be reduced by weak reductants (including organoamines and phenols) that transfer hydrogen atoms to form $L_6Mn_4O_2$ and two water molecules derived from the core oxygen atoms (Scheme 1 path b).[11] Taken together these two reactions indicate a pathway for oxidizing water to O_2 that has the potential to be catalytic if the cycle can be closed.[5, 6]

Only two other manganese complexes have provided evidence for O_2 production from water. A covalently linked perfluorinated dimangano–porphyrin complex was reported to electrochemically oxidize water via O–O bond coupling within an unobserved $(Mn^V{=}O)_2$ intermediate, prior to oxidative destruction.[12] Also, $[(terpy)(H_2O)Mn(\mu\text{-}O)_2Mn(terpy)(H_2O)]^{3+}$ (terpy = 2,2′:6′,2″-terpyridine) was reported to produce O_2 from oxidized precursors, such as hydrogen persulfate (H_2SO_5) or hypochlorite (ClO^-), by nucleophillic addition to an unobserved $Mn^V{=}O$ intermediate, prior to catalyst destruction.[13, 14] However, in neither of these examples has the mechanism of O–O bond formation been conclusively established, nor are they likely to be a close model for the WOC.

Herein, we compare the photochemistry of manganese–oxo complexes having Mn_2O, Mn_2O_2, and Mn_3O_4 core types to that of the Mn_4O_4 cubane core. We find that the cubane core is unique in its ability to form O_2, and does so by selective rearrangement (without decomposition) to a complex with an Mn_4O_2 butterfly core.

For this study we have synthesized a new derivative of the cubane complex, $L'_6Mn_4O_4$ (**1′**), containing the facially bridging bis(tolyl)phosphinate ligand, $(MePh)_2PO_2^-$.[15] Importantly, **1′** is 100 times more soluble than **1** in nonpolar solvents, which permits concentrations up to ~40 mM in CH_2Cl_2. For mass spectrometric studies all the complexes were dissolved in a volatile organic solvent (CH_2Cl_2, CH_3OH) and deposited on a gold substrate prior to evaporation to dryness. Laser desorption/ionization mass spectrometry (LDI-MS) (excitation at 337 nm, 1 ns duration, power = 1.2–7.9 μJ) and quadrupole mass spectrometry (Q-MS) (excitation at 355 nm, 14 ns duration, power = 500 μJ; excitation at 532 nm, power = 3.3 mJ) were performed as previously described for mass detection of ions (*m*/*z* 150–2000 amu) and neutrals (< 40 amu), respectively.[8]

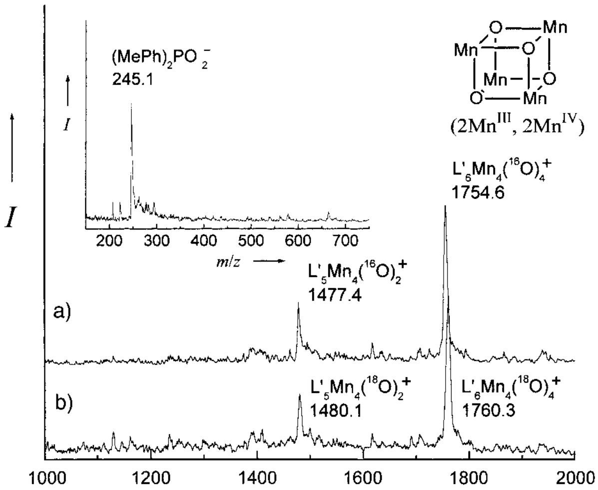


Figure 1. LDI-MS (positive ions) of a) $L'_6Mn_4O_4$ and b) $L'_6Mn_4(^{18}O)_4$ with 75 % labeling of core oxo groups by ^{18}O. Excitation by N_2 laser at 337 nm; power = 2.9 μJ and 4.3 μJ for (a) and (b), respectively). Inset shows LDI-MS (negative-ions) of $L'_6Mn_4O_4$. The ordinate axis is intensity (*I*: arbitrary units).

The positive-ion LDI-MS spectrum of **1′** produces only two peaks above *m*/*z* 150 (Figure 1 a) at *m*/*z* 1754.6 and 1477.4. The first peak corresponds to the parent cation $\mathbf{1'}^+$ (exact *m*/*z* 1755.2), while the latter peak is assigned to $L'_5Mn_4O_2^+$ (*m*/*z* 1477.9) arising from loss of one $(MePh)_2PO_2^-$ ligand (mass 245.2) and two O atoms from **1′**. These assignments are corroborated by the LDI-MS spectrum of the $L'_6Mn_4(^{18}O)_4$ isotopomer (Figure 1 b), in which the Mn_4O_4 core oxo units were replaced by ^{18}O atoms.[16] Only these two peaks were detected at all laser energies available (< 4 μJ pulse^{-1}). The peak height of the fragment peak (*m*/*z* 1447.9) increases, while the parent ion peak (*m*/*z* 1755.2) decreases with laser pulse energy. Data supporting this correlation were previously published for the diphenyl derivative **1**.[8] This trend was attributed to the competition between decay of the excited state **1*** to the ground state **1** and the photochemical reaction given in [Eq. (1)].

$$L_6Mn_4O_4 \leftarrow L_6Mn_4O_4^* \rightarrow L_5Mn_4O_2^+ + L^- + O_2 \qquad (1)$$

Consistent with the fragmentation pattern in Figure 1, the negative-ion LDI-MS of **1′** revealed only a single major peak at *m*/*z* 245.1 in the range *m*/*z* 150–750, corresponding to the $(MePh)_2PO_2^-$ ligand (inset Figure 1). This photofragmentation pattern is identical to that observed for **1** prepared using $Ph_2PO_2^-$ as bridging ligand.[8] The Q-MS of **1′** (Figure 2 a) reveals that the photoreaction releases an O_2 molecule[17] and there is no evidence for any other oxygen-derived products (O, OH, OH_2).[18] Thermodynamic estimates indicate that the O–O bond enthalpy should contribute greatly

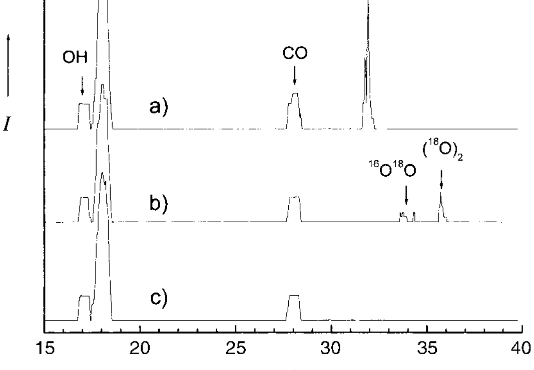


Figure 2. Q-MS of a) $L'_6Mn_4O_4$, b) $L'_6Mn_4(^{18}O)_4$ with 75 % labeling of the core oxo groups by ^{18}O, and c) background (no complex). Internal standard peaks at *m*/*z* 17, 18, and 28 are from OH, H_2O, and CO. Excitation by Nd-YAG laser at 355 nm. The ordinate axis is intensity (*I*: arbitrary units).

(119 kcal mol^{-1}) to lowering the barrier to O_2 release.[8, 11] The data for the $L'_6Mn_4(^{18}O)_4$ isotopomer (Figure 2b) reveals that the product O_2 is derived exclusively from the intramolecular combination of core oxo units; none of the oxygen atoms of $(MePh)_2PO_2^-$ appear in the product O_2. These results explicitly show that laser UV excitation initiates a photochemical reaction in the gas phase (Scheme 1 path a). The relative quantum yield for O_2 production from **1**′ increases with laser pulse energy and reaches 60% (not shown) at the maximum laser energy (7.9 μJ) available in our spectrometer (Table 1). These results extend the generality of the photochemistry previously observed with the first cubane complex **1** and summarized in Scheme 1 path a.

To determine if analogous photochemistry is observed with other manganese–oxo clusters the same experiments were carried out using the series of di- and trimanganese–oxo complexes[19] listed in Table 1. This includes complexes having different bridging groups: di(μ-oxo), di(μ-oxo)-mono(μ-carboxylato), and mono(μ-oxo)-di(μ-carboxylato) and different formal oxidation states of the Mn ions: (III, III), (III, IV) and (IV, IV, IV). Although all complexes absorb intensely at both UV excitation wavelengths (355 nm, and 337 nm), none of them produce molecular O_2 in significant yield when compared to the cubanes **1** and **1**′. LDI-MS reveals that these complexes do undergo laser-induced desorption and photoreactions at these wavelengths, leading to multiple fragments in the gas phase which vary with the laser power (not shown). However, the photo-products correspond to nonselective destruction of the complexes into multiple fragments. This is illustrated by the positive-ion LDI-MS spectrum of $[(bpy)_2Mn(\mu\text{-}O)_2Mn(bpy)_2](C1O_4)_3$ (**2**; bpy = 2,2′-bipyridine) shown in Figure 3. One observes five photo-induced intense peaks in the rage of *m/z* 100–2000. These correlate with the fragments derived from the decomposition of the core and ligands (Table 2). Neither a peak for the parent ion peak (*m/z* 255.5), nor for the intact core Mn_2O_2 fragment is detected. Rather, the preferred fragmentation leads to oxygen atoms which are detected exclusively in the two peaks assigned to $[(bpy)_nMnO_2]^+$ ($n = 1, 3$). Thus, the dimeric $[Mn_2O_2]^{3+}$ core complex does not photorearrange to release O_2 despite having the same Mn oxidation state (Mn^{III}, Mn^{IV}) as **1**′; nor do any of the other core topologies shown in Table 1 containing the $[Mn(\mu\text{-}O)Mn]^{4+}$, $[Mn(\mu\text{-}O)_2Mn]^{3+}$, or $[Mn(\mu\text{-}O)_2Mn(\mu\text{-}O)_2Mn]^{4+}$ cores.

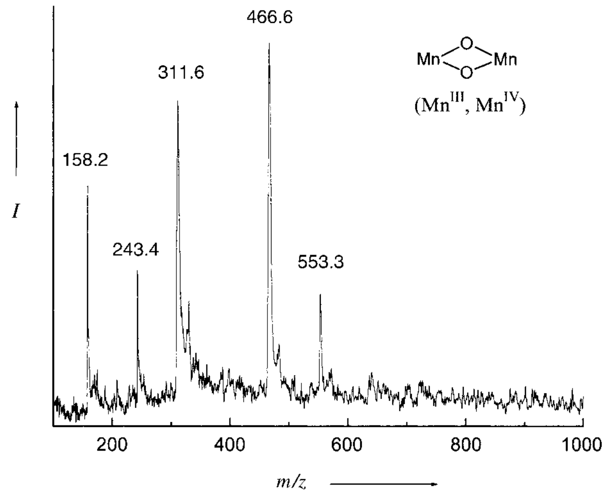


Figure 3. LDS-MS (positive-ions) of $[(bpy)_2Mn(\mu\text{-}O)_2Mn(bpy)_2](C1O_4)_3$. The ordinate axis is intensity (*I*: arbitrary units).

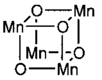
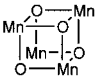
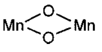
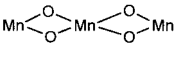
Table 2. Proposed assignments of LDI mass fragment peaks for $[(bpy)_2Mn(\mu\text{-}O)_2Mn(bpy)_2](ClO_4)_3$.

m/z[a]	Fragment	predicted *m/z*
158.2 ± 2.0	$bpyH^+$	157.2
243.4 ± 1.3	$[MnO_2(bpy)]^+$	243.1
311.6 ± 12.7	$[2bpy - H]^+$	311.4
466.6 ± 10.7	$[3bpy - 2H]^+$	466.5
553.3 ± 2.5	$[MnO_2(3bpy - 2H)]^+$	552.5

[a] *m/z* range denotes the full width at half height.

Laser excitation in the visible absorption band at 532 nm (14 ns duration, power = 3.3 mJ) failed to produce O_2 from any of the complexes given in Table 1, including **1** and **1**′, even at a six-fold higher pulse energy than at 355 nm (no Q-MS

Table 1. Structures of Mn complexes used, photochemical O_2 yield and asymmetric vibration energies of the Mn-O-Mn core.

	Complex[a]	Oxidation state	Core geometry	Excitation wavelength [nm]	O_2 quantum relative yield[%][b]	Mn-O-Mn ν_{as} [cm^{-1}]
1	$L_6Mn_4O_4$	($2Mn^{III}$, $2Mn^{IV}$)		355	60[c]	633
				532	0	
1′	$L'_6Mn_4O_4$	($2Mn^{III}$, $2Mn^{IV}$)		355	60[c]	633
				532	0	
2	$[(bpy)_2Mn(\mu\text{-}O)_2Mn(bpy)_2](ClO_4)_3$	(Mn^{III}, Mn^{IV})		355	0	690
				532	0	
3	$[(HBPz_3)Mn(\mu\text{-}O)(\mu\text{-}RCO_2)_2Mn(HBPz_3)]$	($2Mn^{III}$)	Mn—O—Mn	355[d]	0	716[d]
				532[d]	0	
				355[e]	0	717[e]
				532[e]	0	
4	$[(HBPz_3)Mn(\mu\text{-}O)_2(\mu\text{-}RCO_2)Mn(\mu\text{-}O)_2(\mu\text{-}RCO_2)Mn(HBPz_3)]$	($3Mn^{IV}$)		355[d]	0	702[d]
				532[d]	0	

$L = Ph_2PO_2^-$, $L' = (MePh)_2PO_2^-$, bpy = 2,2′-bipyridine, $HBPz_3^-$ = hydrotris(1-pyrazolyl)borate; [a] The number of moles the complex used in each experiment is constant. [b] The zero quantum yield indicates values less than the detection limit for O_2 based on the sensitivity for O_2 detection from **1**′ (< 3.7%). [c] The yield was taken as the ratio of LDI-MS peak heights ($L'_5Mn_4O_2/L'_6Mn_4O_4$). [d] $R = CH_3$, [e] $R = C_2H_5$.

peaks at all!). Hence, the UV photoproduction of O_2 occurs exclusively for the Mn_4O_4 cubane core type upon excitation of the O →Mn charge-transfer absorption at 300 nm ($\varepsilon = 2.1 \times 10^4\,\text{M}^{-1}\text{cm}^{-1}$), but not the visible band at 498 nm ($\varepsilon = 1.4 \times 10^3\,\text{M}^{-1}\text{cm}^{-1}$).[8]. We may conclude that of the complexes listed in Table 1 only the Mn_4O_4 cubane core topology provides a favorable geometry for efficient and selective photorearrangement to produce O_2 by charge-transfer excitation. The $L'_5Mn_4O_2$ photoproduct of **1′** (see below) is presumed to have a "butterfly" core geometry (Scheme 1). The gas-phase structure is unknown, and is only suggested based on comparison to the deoxygenated product, $L'_6Mn_4O_2$, produced in solution by chemical reduction.[11]

Importantly, no mass spectral evidence is found for the photochemical O_2 release from excited **1′** without the loss of one $(MePh)_2PO_2^-$ ligand, nor of ligand release without the loss of O_2. The release of O_2 to form the pinned butterfly structure $L'_6Mn_4O_2$ is thermodynamically favored by $-6.2\,\text{kcal mol}^{-1}$ in the ground state, but is not observed because of a kinetic barrier that the present data show to be imposed by the phosphinate bridges.[8] The origin of the selective O_2 release observed for the photo-excited Mn_4O_4 cubane core appears to correlate with the considerably weaker Mn–O (core) bonds, as found by both X-ray diffraction (mean bond length 1.95 Å for **1** versus 1.8 Å for the Mn_2(III, IV) complex **2**, both in their ground states) and by their much lower-energy Mn-O-Mn core vibrations ($\tilde{\nu}_s = 516\,\text{cm}^{-1}$, $\tilde{\nu}_{as} = 633\,\text{cm}^{-1}$ for the symmetric and asymmetric modes stretches in the ground state) versus the model complexes in Table 1. The inter-oxygen separation in the core of **1** and **1′** is 2.53–2.60 Å which is much longer than the O–O bond in hydrogen peroxide (1.50 Å) and O_2 (1.21 Å). Thus, it is clear that an O–O bond of appreciable stability can not be formed in the ground-state cubanes without large-scale distortion. The experimental data points to the release of a phosphinate bridge and further weakening of the O–Mn bonds in the photo-excited state as the trigger that enables the distortion of the core bonds to occur. The resulting distortion might then permit the oxygen atoms to move sufficiently close together to allow the large intermolecular O–O bond enthalpy ($-36\,\text{kcal mol}^{-1}$ in HO–OH) to contribute to lowering the activation barrier for O_2 formation. By contrast, the much stronger and shorter Mn–O bonds within the planar Mn_2O_2 rhombohedra of the dimer and trimer complexes in Table 1 may be why these core types photodecompose to MnO_2X fragments without Mn–O bond cleavage or O_2 formation.

EPR spectroscopy indicates that cubanes **1** and **1′** have the same oxidation state as the so-called S_3 state of the WOC, or one-electron below the S_4 state that is the precursor to thermal O_2 release.[9, 10] This assignment is debatable particularly in light of data from X-ray absorption near-edge spectroscopy.[10] It will be interesting to see if the one-electron oxidized cubanes $\mathbf{1}^+$ and $\mathbf{1}'^+$, which have been isolated,[20] will also prove to be selective precursors to photolytic and/or thermal evolution of O_2. Based on EPR and X-ray absorption spectroscopic evidence distorted Mn_4O_4 cubane or $Mn_4O_2X_2$ pseudo-cubane cores have been implicated as possible core types for the S_3 and S_4 states of the WOC.[10] The present study indicates a molecular basis for why the cubane core topology appears to be uniquely suited for O_2 evolution.

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[15] **1′** was synthesized according to the earlier reported synthesis of **1**[21] by replacing Ph_2PO_2H with $(MePh)_2PO_2H$ (65% yield). $(MePh)_2PO_2H$ was prepared by the Grignard reaction of MePhMgBr with Et_2N-$POCl_2$ according to the literature.[22] The ^1H NMR, MS, FT-IR, and electronic spectra indicate a symmetrical cubane core very similar to **1**.[21]
[16] Synthesis of $L'_6Mn_4(^{18}O)_4$ was performed starting from $[Mn_2(^{18}O)_2(bpy)_4](ClO_4)_3$ achieved by acid catalyzed exchange against 99% ^{18}O-enriched water. The incorporation of av. 75% ^{18}O was confirmed by FT-IR and LDI-MS analysis.
[17] Upon photoexcitation of **1′** only a single peak was observed at *m/z* 32 corresponding to $(^{16}O)_2$. For $L'_6Mn_4(^{18}O)_4$ (av. 75% isotopic enrichment) two peaks at m/z 34 and 36 were observed, corresponding to $^{16}O^{18}O$ and $(^{18}O)_2$, respectively.
[18] Atmospheric H_2O and CO_2 in the mass spectrometer produce a constant background signal (Figure 2c), while photoproduced species can be distinguished by a "spike" appearance in the mass scan. The spikes arise as a result of the short laser pulse, which produces transient mass changes on a much shorter time scale than the slower sweep rates of the mass analyzer.
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