Water oxidation by a biomolecule (amavadin) without light contribution

Amavadin is a metallobiomolecule without amino acids that occurs with a significant concentration in a few closely related *Amanita* fungi, such as *A. muscaria*. It is a $[V(S,S\text{-}HIDPA)_2]^{2-}$ complex anion (see Figure 1, assigned with A) with vanadium(IV) coordinated by two fully deprotonated (S,S)-*N*-hydroxyimino-(2,2')-dipropionate ligands. This complex does not exhibit an oxovanadium (V=O) group, in contrast to typical vanadium complexes with oxidation state four, and the metal is bound to eight different atoms, what is uncommon for the early transition metals of the Periodic Table. The biological role of amavadin is yet undisclosed, but it exhibits peroxidase- (concerning biological thiols, e.g., cysteine and glutathione) and catalase-type activities.

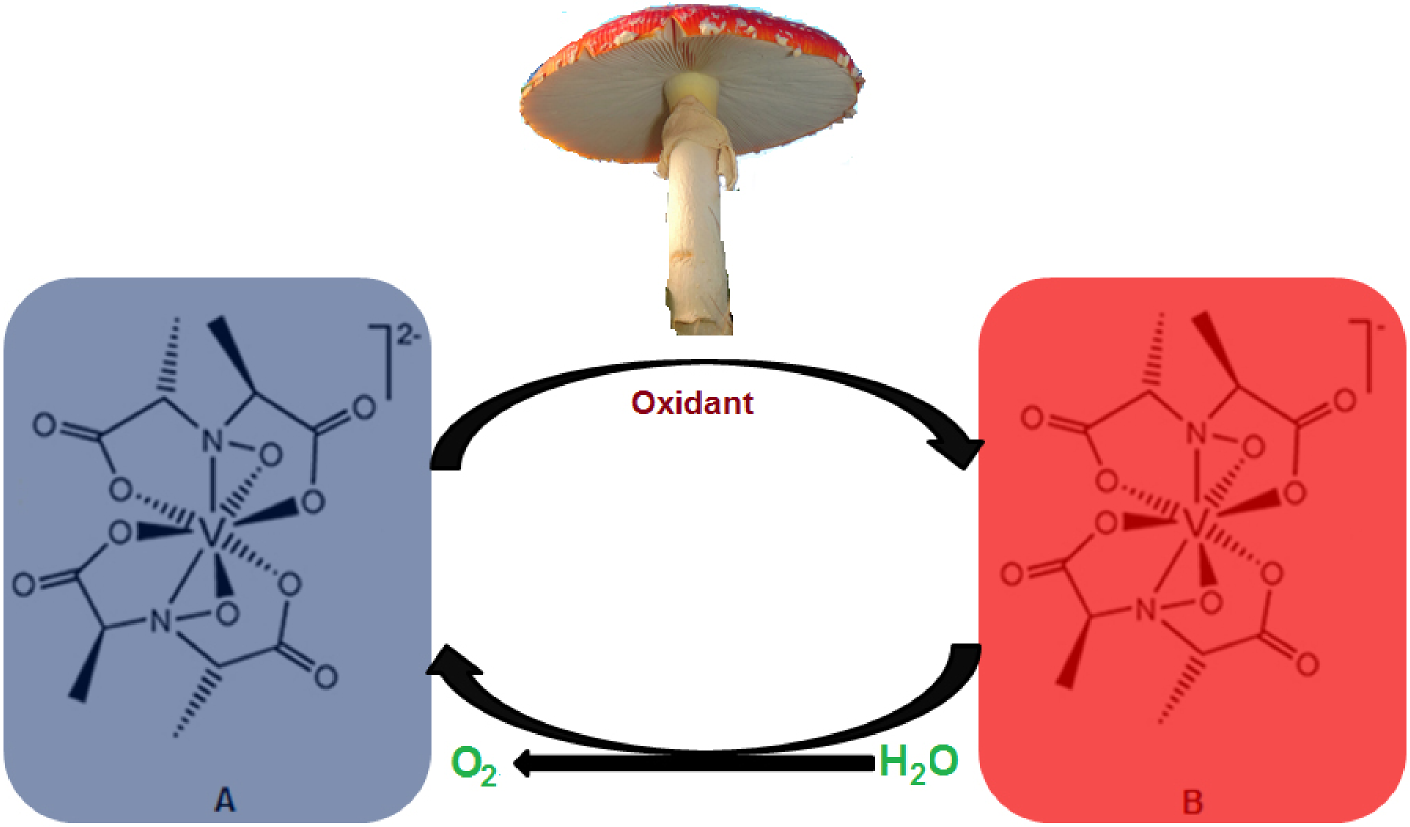

Fig. 1. Amavadin as mediator of water oxidation without light contribution

Water oxidation potentially can supply alternative solutions to cover the energy demands in the future, and also for *in situ* treatment of waters or air regeneration in enclosed spaces. Biologically, water oxidation is carried out by photosystem II (by the majority of the autotrophic organisms, but not the heterotrophic ones), which contains in the active center a manganese cluster, and is dependent on light radiation. To achieve water oxidation by chemical models, several transition metal (from groups 7-11 of Periodic Table) compounds have been studied by using primary oxidants. Alternatively, electrochemical, photochemical, electrophotochemical and thermal approaches have been employed for the same purpose.

Amavadin (see above) and its homologues (with hydroxyimino dicarboxylate ligands) are the first complexes up to the Group 7 of Periodic Table that mediate water oxidation, without requiring light radiation as activator. Amavadin is the second found metallobiomolecule that mediates such a reaction, after photosystem II which, however, requires radiation exposure. The overall reaction leads to the release of molecular oxygen for both metallobiomolecules.

In the case of amavadin the pathway starts by addition of a suitable oxidant to an aqueous solution containing the metallobiomolecule that oxidizes the blue vanadium(IV) metal center to a red vanadium(V) species – the complex of Figure 1 assigned with B). Subsequently, it returns from red to the initial blue, forming the original complex (Fig. 1). During this transition, evolution of small gas bubbles occurs, which are rich in molecular oxygen.

Water oxidation mediated by amavadin involves a new type of mechanism. The reaction is achieved by the cooperation of a single metal and ligand (the oxyimino group), with the metal oxidation state variation of only one unit. In the previously studied systems, the metal could change its oxidation state by more than one unit or the system comprised more than one metal center. Therefore, the amavadin structure and its mechanism for water oxidation can lead to the design of a new type of complexes as catalysts for this reaction, as well as to other oxidation reactions, taking into account the capacity of amavadin to act as catalyst for several oxidation reactions, including hydroxylation, oxygenation, peroxidative halogenation of hydrocarbons, carboxylation of alkanes, oxidation of thioanisole and alcohols, and epoxidation of allylic alcohols. Additionally, the molecular oxygen formation mediated by amavadin can eventually be linked to a biological role, once this product participates in some metabolic reactions of the *A. muscaria* fungus (it is noteworthy that this species belongs to a kingdom whose members are heterotrophs).

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