X-ray Structures of Methylamine Dehydrogenase Reaction Intermediates

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Methylamine dehydrogenase (MADH) is a soluble periplasmic $\alpha_2\beta_2$ heterotetrameric enzyme, present in many methylotropic bacteria, that catalyzes the oxidation of methylamine to formaldehyde and ammonia. It is upregulated by the presence of substrate, and enables bacterial growth on methylamine as the sole carbon, nitrogen and energy source. The redox center is trytophan tryptophylquinone (TTQ) which is composed of two Trp residues that are posttranslational modified by the addition of two oxygens to form an O-quinone and a covalent cross-link. Amicyanin (a type I blue copper protein) is the redox partner of MADH and it is also induced in the presence of methylamine. The reaction during turnover gives distinct spectral features in the visible region, which define specific electronic states of the cofactor.

The use of single crystal kinetics, microspectrophotometry and X-ray crystallography of the holo- (with Cu) and apo- (without Cu) complexes of MADH with amicyanin allows the trapping of different catalytic intermediates in the crystal, and the determination of their x-ray structures. In this presentation the structural features of O-quinone, N-quinol and N-semiquinone catalytic intermediates will be discussed in terms of the current model for catalysis and electron transfer.

Keywords: quinoprotein, redox enzyme, single crystal microspectrophotometry