

## THE Co-N BOND CLEAVAGE IN THE ADENOSYNCOBALAMIN COFACTOR IN ADVANCE TO GLUTAMATE MUTASE AND METHYLMALONYL-CoA MUTASE PROCESSES

Tudor Spataru 

Department of Chemistry, Columbia University, 3000, Broadway, New York, New York 10027, USA  
Natural Sciences Department, Hostos Community College, 500, Grand Concourse, Bronx, New York 10451, USA  
e-mail: [ts2407@columbia.edu](mailto:ts2407@columbia.edu); phone: 1-646-338-5121; fax: 1-212-932-1289

**Abstract.** The *in vivo* experiments show that the adenosylcobalamin cofactor in glutamate mutase and methylmalonyl-CoA mutase processes lose its dimethylbenzimidazole axial ligand before starting the enzymatic processes. Complete active space self-consistent field geometry optimization of the vitamin B12 active forms plus substrates joint models have been performed. These joint models include the adenosylcobalamin cofactor, the carboxyl negative ion model of the studied processes' active substrates, and the histidine molecule. Partial electronic density is transferred from the highest occupied substrate molecular orbitals to the lowest unoccupied antibonding molecular orbitals, which consist of corrin ring and dimethylbenzimidazole ligand common molecular orbitals during the multi-configurational self-consistent field molecular orbital mixing process. As a result, the Co-N axial bond is permanently elongated during the complete active space self-consistent field geometry optimization until its complete rupture and until the removal of the dimethylbenzimidazole ligand from the central cobalt atom and the corrin ring is complete. The Co-N bond cleavage in the adenosylcobalamin cofactors in the studied processes is running as no energy barrier process under the influence of their active substrates and histidine molecule.

**Keywords:** glutamate mutase, methylmalonyl-CoA mutase, adenosylcobalamin cofactor, vitamin B12, Pseudo-Jahn-Teller effect.

Received: 12 July 2023/ Revised final: 19 October 2023/ Accepted: 23 October 2023

---