

Toward quantitatively accurate calculation of the redox-associated acid-base and ligand binding equilibria of aquacobalamin

Challenge

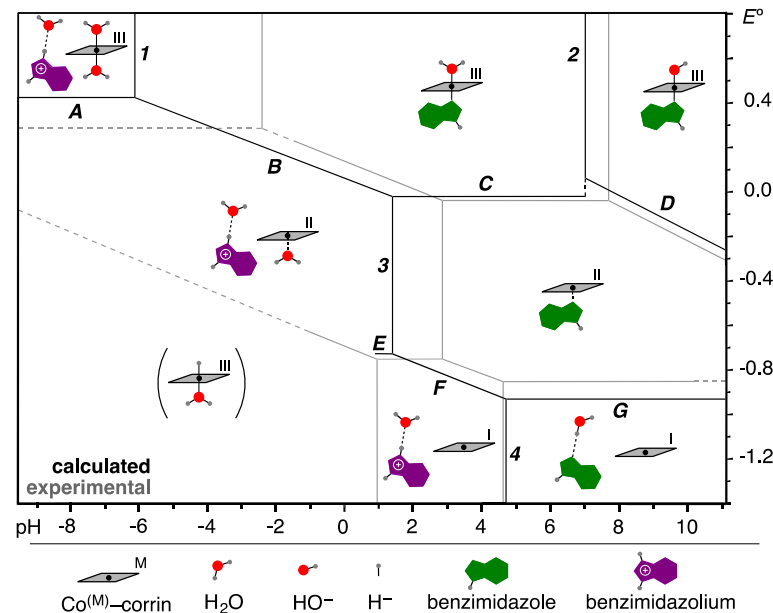
- Develop consistent computational approach for computing pH-dependent redox and ligand dissociation properties of a complex corrinoid cofactor.

Approach and Results

- Used density functional theory (DFT) and continuum solvation to compute Co–ligand binding equilibrium constants ($K_{\text{on/off}}$), $\text{p}K_{\text{a}}$ s and reduction potentials for models of aquacobalamin in aqueous solution.
- RMS errors of 80 mV for seven reduction potentials, 2.0 log units for five $\text{p}K_{\text{a}}$ s and 2.3 log units for two log $K_{\text{on/off}}$ values for aquacobalamin.

Significance and Impact

- Methods will lead to insight into the mechanism of Hg methylation by HgcA, which uses a corrinoid cofactor.
- This approach is more broadly applicable to modeling and simulation of complex subsurface redox processes.



Experimental (gray) and computed (black)
E-pH diagram for aquacobalamin

Participants:

Ryne C. Johnston (ORNL), Jing Zhou (UTK), Jeremy C. Smith (UTK/ORNL), and Jerry M. Parks (ORNL)

Contact: parksjm@ornl.gov

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