

SUPPORTING INFORMATION

**Characterization of Protein Contributions to Cobalt-Carbon Bond Cleavage
Catalysis in Adenosylcobalamin-Dependent Ethanolamine Ammonia-Lyase by
using Photolysis in the Ternary Complex**

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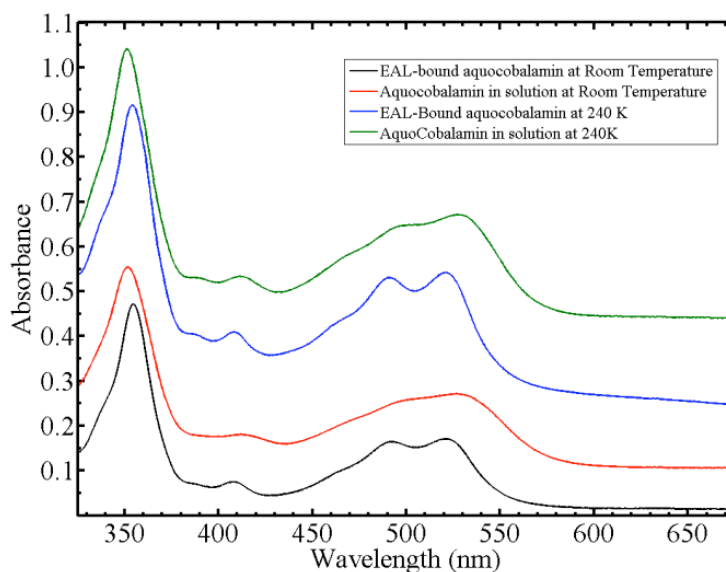


Figure S1. The UV/visible absorption spectra of the cofactor analog, aquocobalamin, in free solution and in the presence of EAL. The paired spectra for aqueous solution (10 mM potassium phosphate, pH=7.5) at 295 K (top), and for the 50% DMSO/water cryosolvent system at 240 K (bottom) are shown. Binding of aquocobalamin to EAL induces spectral changes, that are consistent with the formation of hydroxocobalamin in the protein site, at 295 K. The same spectral characteristics are observed in the cofactor analog at 240 K in the presence of EAL. The spectra also display enhanced resolution for the cobalamin in situ, relative to in solution. The results indicate that the AdoCbl cofactor is stably bound to EAL at low temperature in the cryosolvent system.

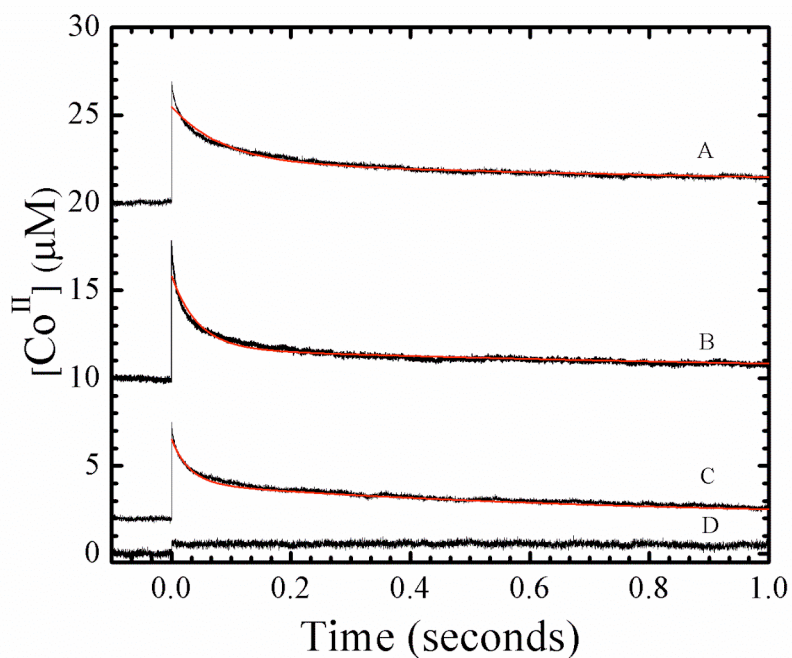


Figure S2. Time dependence of cob(II)alamin concentration following pulsed laser photolysis of adenosylcobalamin (AdoCbl) at 240 K, and overlaid best-fit bi-exponential decay functions (red). The cob(II)alamin concentration was obtained from the absorbance at 470 nm. (A) EAL in aerobic solution. (B) EAL in aerobic solution, with (*S*)-2-amino-1-propanol bound (ternary complex). (C) EAL in aerobic solution, with (*S*)-1-amino-2-propanol bound (inhibitor complex). (D) Anaerobic solution.

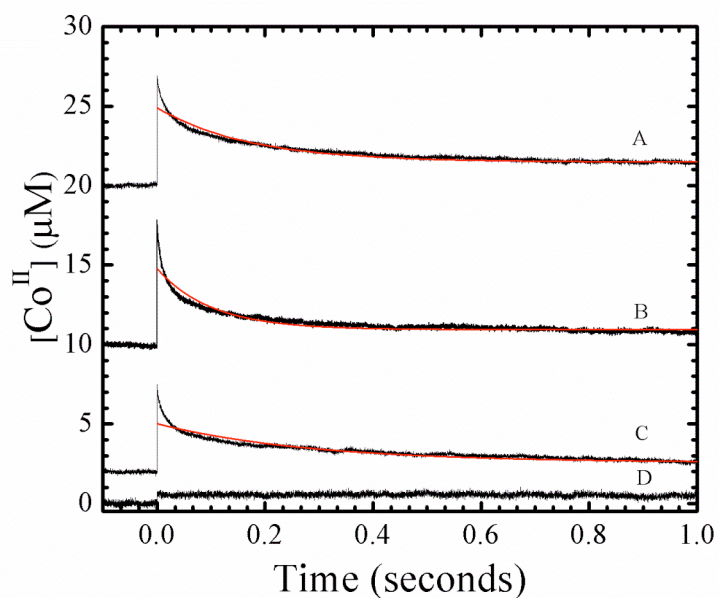


Figure S3. Time dependence of cob(II)alamin concentration following pulsed laser photolysis of adenosylcobalamin (AdoCbl) at 240 K, and overlaid best-fit monoexponential decay plus a constant functions (red). The cob(II)alamin concentration was obtained from the absorbance at 470 nm. (A) EAL in aerobic solution. (B) EAL in aerobic solution, with (*S*)-2-amino-1-propanol bound (ternary complex). (C) EAL in aerobic solution, with (*S*)-1-amino-2-propanol bound (inhibitor complex). (D) Anaerobic solution.