

# Interactions Between a Cyclic Peptide and Cytochrome *c*: Evidence for the Formation of Two Encounter Complexes

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Electron-transfer (ET) reactions occur between a negatively charged cyclic metalloprotein [Ru(bpy)<sub>2</sub>(phen-am)-*cyclo*(Cys-Glu-D-Glu-Glu-Pro-Glu-D-Glu)]<sup>3-</sup> = Rucyclic, and ferricytochrome *c* = Cyt *c*, in which an acetamido linker was used to attach the ruthenium polypyridyl complex to the cysteine side chain of a head to tail cyclic peptide. Photoinduced electron transfer can occur via parallel pathways that involve two different encounter peptide-protein complexes. That the ET rate constants of both encounter complexes decrease with increasing viscosity demonstrates that the kinetics are gated by rate-limiting configurational changes occurring within the complexes.

NMR experiments confirm that two separate conformations exist for Rucyclic. The two conformations of Rucyclic might be arising from the *cis/trans* isomerization of proline and result in the formation of two encounter complexes when interact with Cyt *c*.

