Catechol Dioxygenases

- enzymes in soil bacteria, last step of biodegradation of aromatics
- converts catechol (α-dihydroxybenzene) to acyclic compound used as C source
- two classes, differ in active site, reaction mechanism, regiochemistry of ring cleavage

**Intradiol dioxygenases**
- e.g. 3,4-PCD, 1,2-CTD
- 24 subunits, α₁₂β₁₂ dodecamer
- Fe₃⁺(Nhis)₂(Otyr)₂ active site
- catechol binds as 2⁻ anion, displaces Otyr
- Fe₃⁺ induces spin density on ring, directs simultaneous attack of O₂ on ring and Fe
- O inserts between diol groups
- diacid product

**Extradiol dioxygenases**
- e.g. 1,2-DHBD (BPhC), 2,3-CTD, 2,3-HPCD
- 4 subunits, α₄ tetramer
- Fe²⁺(Nhis)₂(Oglu) active site
- catechol binds as 1⁻ anion
- O₂ binds to Fe, induces spin density on ring, then O₂ attacks
- O inserts outside diol groups
- acid-carbonyl product (aldehyde or ketone)

Intradiol Dioxygenases

**Protocatechuate-3,4-dioxygenase (3,4-PCD) from P. putida and Ac. Strain ADP1**
- rest state: PDB 4WHP (PNAS 2015)
- 3,4-dihydroxybenzoate bound: PDB 1EOB (Biochemistry 2000)
- structural studies with slow substrate, 4-fluorocatechol (PNAS 2015):
  - Fe²⁺(OOR): PDB 4WHQ
  - Fe²⁺(anyhdride): PDB 4WHR
Extradiol Dioxygenases

*Homoprotocatechuate 2,3-dioxygenase (2,3-HPCD) from B. fuscum*

- rest state, HPCD-bound: PDB 4GHG (*Biochemistry* 2012)
- structural studies with slow substrate, 4-nitrocatechol (*Science* 2007):
  - Fe(II)(O=*)(SQ=*): PDB 2IGA:C
  - Fe(II)(OOR): PDB 2IGA:D
  - Fe(II) product-bound: PDB 2IGA:A