Coordination Chemistry Practice Items

1. In the ferrocyanide ion, the six electrons ferrous ion possesses outside of the argon shell assort into three of the five 3d orbitals, and the two remaining 3d orbitals, one 4s orbital, and three 4p orbitals hybridize to form bond orbitals to receive cyanide electron pairs. The shape of the ferrocyanide ion is

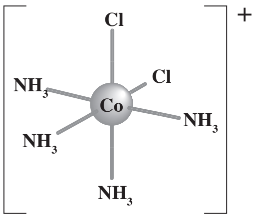
A. trigonal planar
B. tetrahedral
C. trigonal bipyramidal
D. octahedral

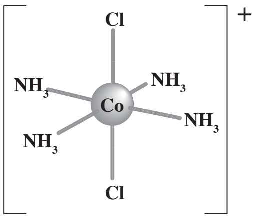
2. A substance which may serve as a ligand in a coordination ion may best be described as a(n)

A. Lewis base
B. nucleophilic anion
C. transition metal
D. electrophilic cation

3. The two complex ions pictured below are

A. optical isomers
B. conformational isomers
C. geometric isomers
D. constitutional isomers





4. A test for silver ion is formation of a precipitate with chloride ion which is soluble in ammonium hydroxide solution. Which compound forms to allow AgCl to dissolve?

A. AgOH
B. NH_4Cl
C. $[Ag(NH_3)_2]^+$
D. AgBr

5. Aqua regia is a mixture of nitric acid and hydrochloric acid that can dissolve gold.

$$\mathrm{Au} + 3\,\mathrm{HNO_3} + 4\,\mathrm{HCl} \longrightarrow [\mathrm{AuCl_4}]^- + 3\,\mathrm{NO_2} + \mathrm{H^+} + 2\,\mathrm{H_2O}$$

What role does chloride play in the process of dissolving gold?

A. conjugate base
B. ligand
C. oxidizing agent
D. reducing agent

6. In aqueous solution, the Ti^{3+} cation exists as the octahedral hydrate $[Ti(H_2O)_6]^{3+}$. Titanium(III) has a single 3d electron. Because two of the d orbitals (d_{x2-y2} and d_{z2}) are nearer to ligand electrons than the other three (d_{xy}, d_{xz}, and d_{yz}), an electron in either of the first two will experience a greater repulsion from ligand electrons. The energy difference for an electron between these two sets of d orbitals is termed the

A. crystal field splitting energy.
B. coordination energy.
C. HOMO to LUMO transition energy.
D. charge transfer transition energy.

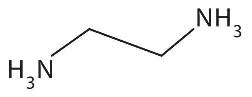
7. Cobalt III forms many octahedral complexes. $[Co(NH_3)_6]^{3+}$ is yellow and $[Co(NH_3)_5Cl]^{2+}$ is violet. Which of the following is the best explanation for the difference in color?

A. the greater d-d transition energy in $[Co(NH_3)_6]^{3+}$.
B. $[Co(NH_3)_6]^{3+}$ is a high spin complex while $[Co(NH_3)_5Cl]^{2+}$ is low spin.
C. the bathochromatic shift due to greater HOMO to LUMO transition energy.
D. the difference in enthalpy of hydration.

8. $Cr_2(SO_4)_3$ is a soluble electrolyte. Dissolving $Cr_2(SO_4)_3$ yields a violet solution. Titrating with NaOH produces a blue-violet precipitate (Compound II). Upon further titration with additional base, the precipitate redissolves as Compound III. Which of the following is Compound III?

A. $[Cr(H_2O)_6]^{3+}$
B. $[Cr(H_2O)_4(OH)_2]^{+}$
C. $[Cr(H_2O)_3(OH)_3]$
D. $[Cr(H_2O)_2(OH)_4]^{-}$

9. Tris(ethylenediamine)cobalt(III) chloride is the chloride salt of the complex ion $[Co(en)_3]^{3+}$ where 'en' is the abbreviation for the bidentate ethylenediamine ligand, pictured below.



What is the coordination number of cobalt in tris(ethylenediamine)cobalt(III) chloride?

A. 2
B. 3
C. 6
D. 8

10. We can arrange ligands in the order of their ability to produce large crystal field splitting energy, Δ. This series is called the spectrochemical series.

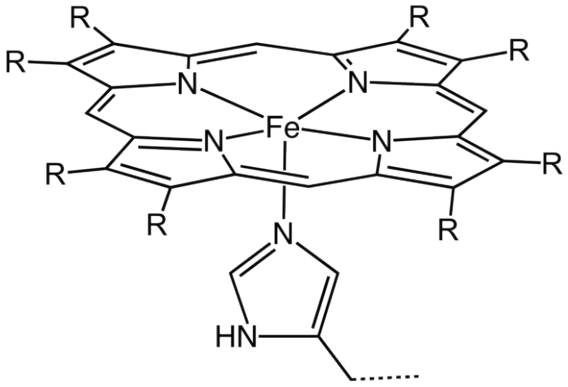
$Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < NO_2^- < CN^-$

Of the following ligands, which has the greatest possibility of producing a diamagnetic complex?

A. NH_3
B. Br^-
C. OH^-
D. Br^-

11 . The iron within the heme prosthetic group of deoxyhemoglobin is in Fe(II). After binding O_2, the iron transfers a single electron to the oxygen, becoming Fe(III). In what form is the oxygen bound to oxyhemoglobin?

A. singlet oxygen
B. triplet oxygen
C. superoxide
D. ozone



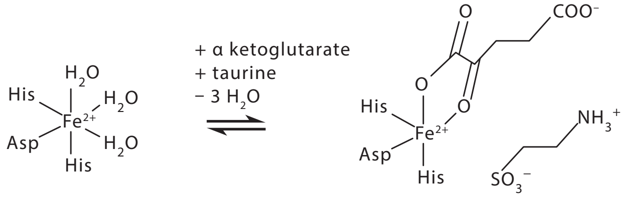
Heme in deoxyhemoglobin

The following passage pertains to questions 12 - 17.

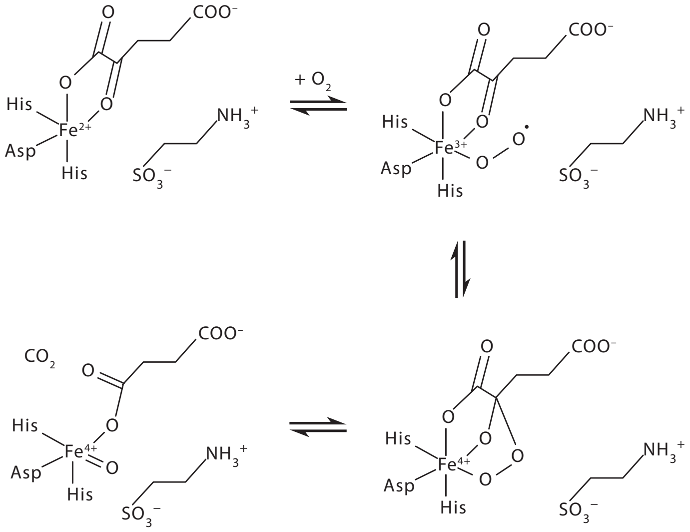
Alpha-ketoglutarate-dependent hydroxylases are non-heme, iron-containing enzymes that consume oxygen and alpha-ketoglutarate as co-substrates. They catalyze a wide range of oxygenation reactions. Functionally, the αKG-dependent hydroxylases are comparable to cytochrome P450 enzymes, which use oxygen and reducing equivalents to oxygenate substrates. In both αKG-dependent hydroxylases and cytochrome P450 enzymes, a high-valent oxoiron(IV) intermediate, first formed through O_2 activation, abstracts a hydrogen from the substrate. The incipient substrate radical is then captured by a hydroxoferric intermediate to afford the hydroxylated product

A typical αKG dependent non-heme iron(II) dioxygenase, TauD, catalyzes the alpha-ketoglutarate-dependent hydroxylation of taurine yielding sulfite and aminoacetaldehyde after decomposition of an unstable intermediate. Expressed as a particular variant in *Escherichia coli* only under conditions of sulfate starvation, TauD is required for the utilization of taurine as an alternative sulfur source for growth in the absence of sulfate.

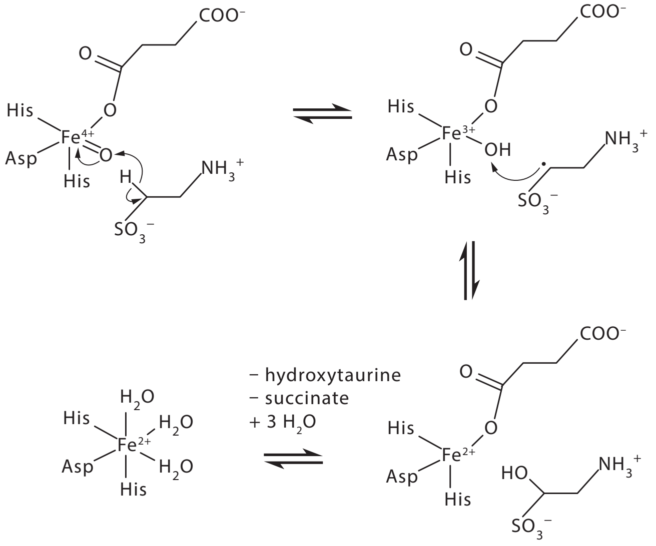
In the active site of TauD, the iron(II) center is coordinated facially by two histidines and one aspartate residue, a motif known as the '2-His-1-carboxylate facial triad'. The first step involves the binding of αKG and taurine to the active site. αKG coordinates to Fe(II) while the taurine substrate is held by noncovalent forces in close proximity.



Subsequently, molecular oxygen binds end-on to Fe cis to the two donors of the αKG. The uncoordinated end of the superoxide ligand attacks the keto carbon, inducing release of CO_2 and forming an Fe(IV)-oxo intermediate.



This Fe=O center then oxygenates the substrate by an oxygen rebound mechanism.



12. Which of the following descriptors accurately characterizes the stereochemical relationship of the two histidine ligands of Fe(II) in the active site of TauD?

- **A.** mer
- **B.** cis
- **C.** octahedral
- **D.** chiral

13. Which of the following binds to the iron cofactor of TauD as a bidentate ligand?

A. histidine imidazole
B. alpha-ketoglutarate
C. taurine
D. superoxide

14. During the ternary complex formation stage of the Tau-D mechanism, the iron cofactor of Tau-D acts as a

A. Lewis acid
B. Lewis base
C. reducing agent
D. ligand

15. Many αKG-dependent dioxygenase enzymes catalyze uncoupled turnover, in which oxidative decarboxylation of αKG into succinate and carbon dioxide proceeds in the absence of substrate. Such enzymes would be dependent on a

A. cytochrome
B. heme cofactor
C. bridging ligand
D. reducing agent

16. The His–Fe(II)–His bond angle in TauD in its unbound state is nearest to which of the following?

A. 60°
B. 90°
C. 109°
D. 120°

17. Which of the following is a characteristic of the low spin d^4 Fe(IV) cofactor attached to the oxo ligand?

I. diamagnetic
II. high crystal field splitting energy
III. tetrahedral geometry

A. I only
B. II only
C. I and II
D. I, II, and III