

## 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

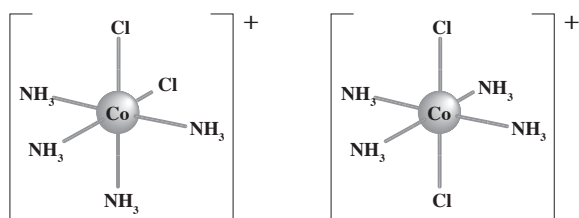
- A. trigonal planar
- B. tetrahedral
- C. trigonal bipyramidal
- D. octahedral

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

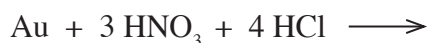
- A. optical isomers
- B. conformational isomers
- C. geometric isomers
- D. constitutional isomers



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<sub>4</sub>Cl
- C. [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>
- D. AgBr

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



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<sup>3+</sup> cation exists as the octahedral hydrate [Ti(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>. Titanium(III) has a single 3d electron. Because two of the d orbitals (d<sub>x<sup>2</sup>-y<sup>2</sup></sub> and d<sub>z<sup>2</sup></sub>) are nearer to ligand electrons than the other three (d<sub>xy</sub>, d<sub>xz</sub>, and d<sub>yz</sub>), 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.

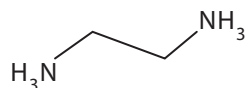
7. Cobalt III forms many octahedral complexes.  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is yellow and  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  is violet. Which of the following is the best explanation for the difference in color?

- A. the greater d-d transition energy in  $[\text{Co}(\text{NH}_3)_6]^{3+}$ .
- B.  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is a high spin complex while  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  is low spin.
- C. the bathochromic shift due to greater HOMO to LUMO transition energy.
- D. the difference in enthalpy of hydration.

8.  $\text{Cr}_2(\text{SO}_4)_3$  is a soluble electrolyte. Dissolving  $\text{Cr}_2(\text{SO}_4)_3$  yields a violet solution. Titrating with  $\text{NaOH}$  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.  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- B.  $[\text{Cr}(\text{H}_2\text{O})_4(\text{OH})_2]^+$
- C.  $[\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3]$
- D.  $[\text{Cr}(\text{H}_2\text{O})_2(\text{OH})_4]^-$

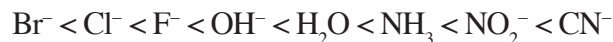
9. Tris(ethylenediamine)cobalt(III) chloride is the chloride salt of the complex ion  $[\text{Co}(\text{en})_3]^{3+}$  where 'en' is the abbreviation for the bidentate ethylenediamine ligand, pictured below.



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,  $\Delta$ . This series is called the spectrochemical series.

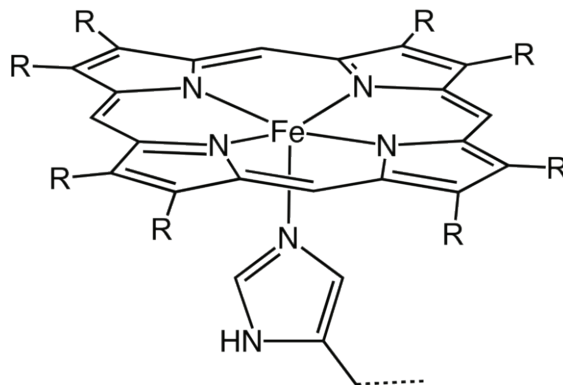


Of the following ligands, which has the greatest possibility of producing a diamagnetic complex?

- A.  $\text{NH}_3$
- B.  $\text{Br}^-$
- C.  $\text{OH}^-$
- D.  $\text{Br}^-$

11. The iron within the heme prosthetic group of deoxyhemoglobin is in Fe(II). After binding  $\text{O}_2$ , 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



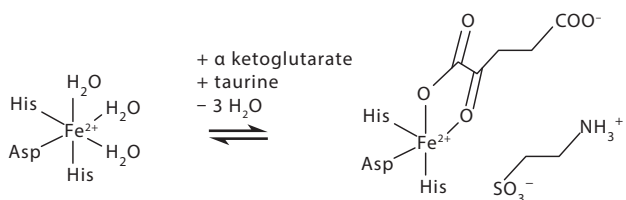
Heme in deoxyhemoglobin

The following passage pertains to questions 12 - 17.

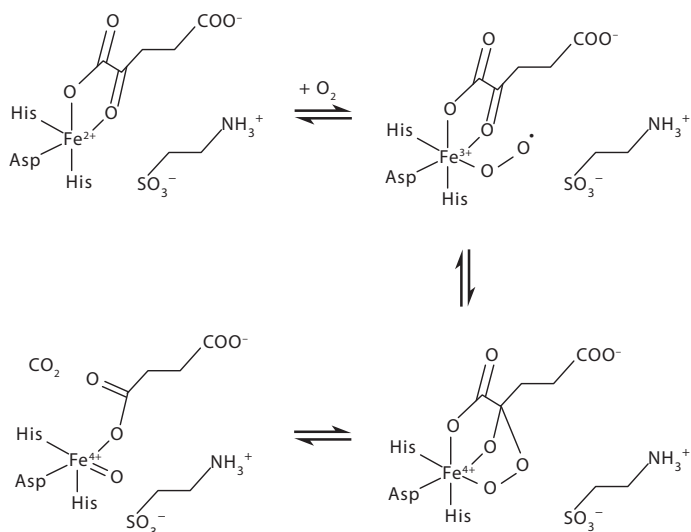
Alpha-ketoglutarate-dependent hydroxylases are non-heme, iron-containing enzymes that consume oxygen and alpha-ketoglutarate as co-substrates. They catalyze a wide range of oxygenation reactions. Functionally, the  $\alpha$ KG-dependent hydroxylases are comparable to cytochrome P450 enzymes, which use oxygen and reducing equivalents to oxygenate substrates. In both  $\alpha$ KG-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  $\alpha$ KG 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.

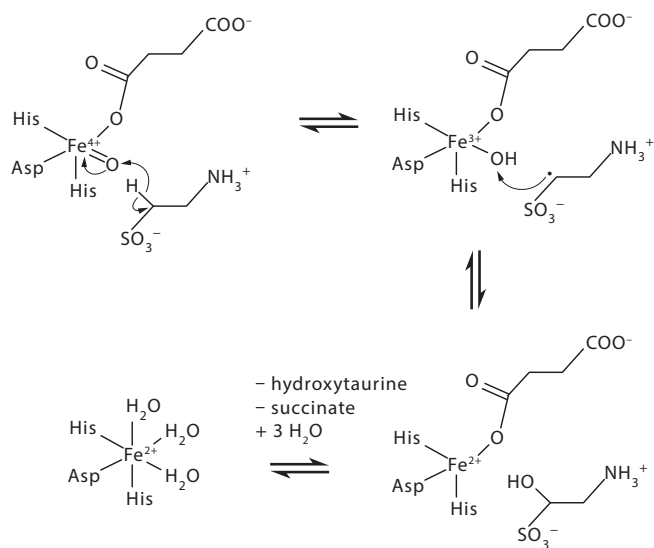
In the active site of TauD, the iron(II) center is coordinated facially by two histidines and one aspartate residue, a motif known as the '2-His-1-carboxylate facial triad'. The first step involves the binding of  $\alpha$ KG and taurine to the active site.  $\alpha$ KG coordinates to Fe(II) while the 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  $\alpha$ KG. 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  $\alpha$ KG-dependent dioxygenase enzymes catalyze uncoupled turnover, in which oxidative decarboxylation of  $\alpha$ KG 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.  $60^\circ$
  - B.  $90^\circ$
  - C.  $109^\circ$
  - D.  $120^\circ$

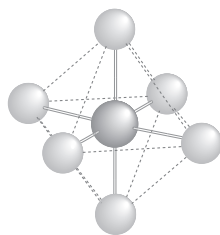
17. Which of the following is a characteristic of the low spin  $d^4$  Fe(IV) cofactor attached to the oxo ligand?
- I. diamagnetic
  - II. high crystal field splitting energy
  - III. tetrahedral geometry
- A. I only
  - B. II only
  - C. I and II
  - D. I, II, and III
-

## Coordination Chemistry

### Answers and Explanations

#### 1. D

The question stem describes a complex ion with coordination number of 6, six cyanide ligands arrayed around a central iron. As described in VSEPR (valence shell electron pair repulsion), when there are six regions of electron density around a central atom, the resulting geometry is octahedral.

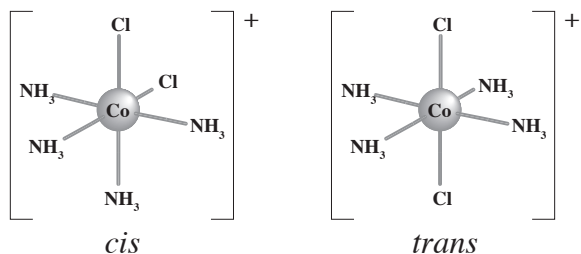


#### 2. A

A ligand is an ion or molecule that binds to a central metal atom to form a coordination complex. The bonding with the metal generally involves the contribution of one or more of the ligand's electron pairs to forming the bond(s) to the metal. A ligand is a Lewis base, in other words, an electron pair donor.

#### 3. C

An octahedral complex such as  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  can exist in a type of stereoisomerism known as geometric isomerism. Geometric isomers are each of two or more compounds which differ from each other in the arrangement of groups with respect to a double bond, ring, or other rigid structure. Just as with geometric isomerism in organic chemistry, in coordination chemistry we can also use the prefixes "cis" and "trans", from Latin, which mean "this side of" and "the other side of", respectively, to distinguish these two geometric isomers.



#### 4. C

Dissolving a weak electrolyte can be facilitated through coupled equilibrium with complex ion formation.

#### 5. D

Neither nitric acid nor hydrochloric acid will dissolve gold alone. Each acid performs a different task in combination in aqua regia. Nitric acid oxidizes gold to form a virtually undetectable concentration of gold ions ( $\text{Au}^{3+}$ ). The hydrochloric acid provides a ready supply of chloride ions ( $\text{Cl}^-$ ), which react with the gold ions to produce tetrachloroaurate(III) anions. In summary, nitric acid acts as an oxidizer and chloride as a ligand in complex ion formation, leading to the removal of gold ions from solution and allowing further oxidation of gold to take place.

#### 6. A

In an octahedral complex, the d orbitals of the central metal ion divide into two sets of different energies. The separation in energy is the crystal field splitting energy.

#### 7. A

Crystal field theory presents a simple model which is useful for explaining the observed color of many, though not all, coordination complexes. In crystal field theory, the ligand electron pairs create an electric field environment. The five d subshell orbitals of the central metal atom are not affected equally by this ligand field. Two of the five d-subshell orbitals in an octahedral complex, for example, are, basically, pressing against a ligand electron pair while the other three are not, so an electron in one of those two orbitals will be at a higher energy than within one of the other three. This is called crystal field splitting. Now that there is an energy difference among the d-subshell orbitals, there is an electronic transition which can correspond to photon absorbance. The absorbed photons tend to be visible.

We were told that the complex ion  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is yellow and  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  is violet. The color you see is not the color absorbed. You are seeing the complement of the color absorbed. If you see yellow, that

means that violet photons are being absorbed, and vice versa. If you see violet color, it means yellow photons were absorbed. Violet photons are higher energy than yellow photons. This corresponds to the greater d-d transition energy in  $[\text{Co}(\text{NH}_3)_6]^{3+}$

### 8. D

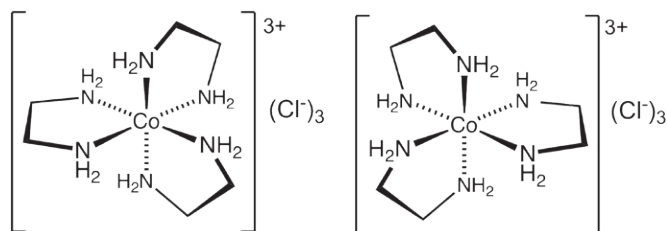
Many transition metal cations actually exist in aqueous solution as a hydrate complex ion. In solution chemistry, we say  $\text{Cr}^{3+}$ , but the actual form is  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ .

The question gives us help in that the answer choices as a whole give us enough to construct the story. Titrating  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (choice 'A') with base, we are replacing  $\text{H}_2\text{O}$  ligands with  $\text{OH}^-$  ligands. Eventually we reach  $[\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3]$  (Compound II, choice 'C'), which is no longer an ion, and so it precipitates. Continuing to titrate with  $\text{OH}^-$  forms  $[\text{Cr}(\text{H}_2\text{O})_2(\text{OH})_4]^-$  (Compound III, choice 'D'), which redissolves.

### 9. C

A bidentate ligand has two atoms that coordinate directly to the central atom in a complex. Ethylenediamine is a bidentate ligand. A single molecule of ethylenediamine can form two bonds to a metal ion. In tris(ethylenediamine)cobalt(III) chloride each of the three ethylenediamine ligands brings two electron pairs to cobalt(III), so the coordination number of cobalt is six, and it is an octahedral complex.

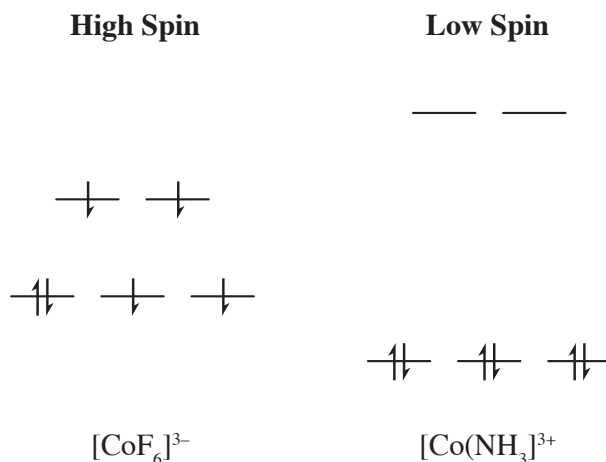
Although this is not an issue for the question, having three bidentate ligands, any tris(ethylenediamine)cobalt(III) complex is not super-imposable on its own mirror image, so there are two enantiomers of the complex.



### 10. C

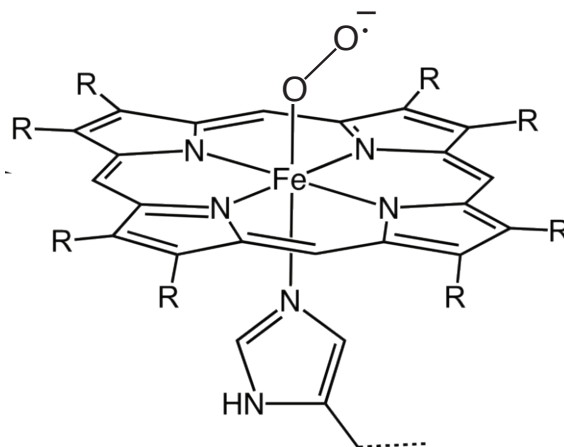
$\text{NH}_3$  is the ligand with the greatest ability to produce a complex with high splitting energy. In a complex with high crystal field splitting energy, the electrons will tend to pair in the lower energy d-subshell orbitals. High splitting energy is consistent with a low spin complex, in other words. If the splitting energy is low, though, there is a tendency for the electrons to go singly into all five orbitals with parallel spin as predicted by Hund's rule.

When there are six d-subshell electrons, a low spin complex will be diamagnetic (all electrons paired).



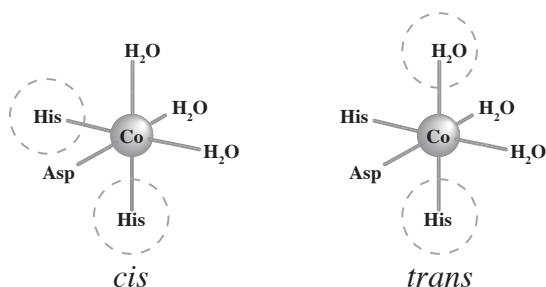
### 11. C

The behavior of heme in hemoglobin is one of the most significant examples of coordination chemistry in biochemistry. The oxygen in oxyhemoglobin is in the form of superoxide radical anion.

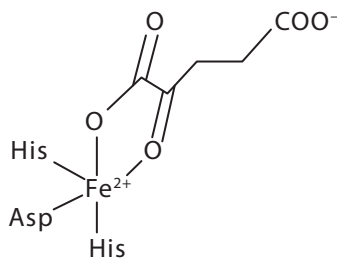


**12. B**

The passage describes the '2-His-1-carboxylate facial triad' in which the two histidine and one aspartate residues coordinate the Fe(II) cofactor facially. When three identical ligands occupy one face, the isomer is said to be facial, or fac. Facially oriented ligands within an octahedral complex will be cis to each other.

**13. B**

Bidentate ligands are Lewis bases that donate two pairs of electrons to a metal atom.  $\alpha$ KG coordinates to Fe(II) as a bidentate ligand.

**14. A**

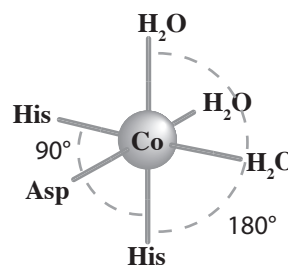
'Ternary complex' is not a term of conceptual vocabulary from coordination chemistry. It's not a kind of coordination complex but a kind of enzyme-substrate complex. A ternary complex is an enzyme-substrate complex formed between two substrate molecules and an enzyme. Multi-substrate enzyme-catalyzed reactions that follow a sequential mechanism will form a ternary complex. In other words, question stem is referencing is the initial substrate binding in which the iron cofactor receives the electron pairs brought by  $\alpha$ KG as a coordinating ligand. A Lewis acid is an electron pair receiver.

**15. D**

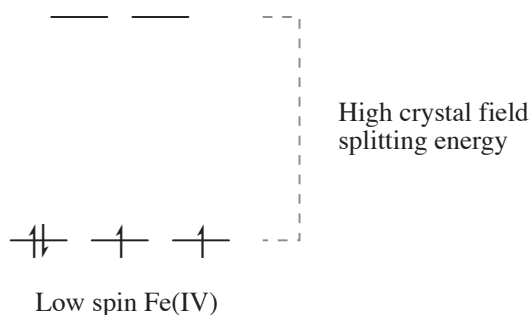
Subsequent to decarboxylation of  $\alpha$ KG the iron cofactor of an  $\alpha$ KG-dependent dioxygenase will be in the Fe(IV) oxidation state. To complete the mechanistic cycle and return the iron to the Fe(II) oxidation state will require a reducing agent.

**16. B**

From VSEPR we know that the bond angles in octahedral geometry are  $90^\circ$  and  $180^\circ$ . The bond angle between two cis ligands in an octahedral complex is  $90^\circ$ .

**17. B**

In a complex with high crystal field splitting energy, the electrons will tend to pair in the lower energy d-subshell orbitals. In other words, high splitting energy produces a low spin complex.



Regarding choice 'I', even though the net spin is lower in this case than if the electrons had been spread out singly with parallel spin among the five d orbitals (high spin), low spin Fe(IV) is still paramagnetic. It would be diamagnetic only if all of the electrons were paired.