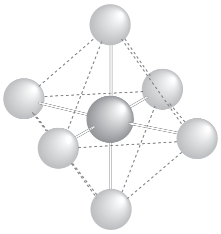
Coordination Chemistry

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.

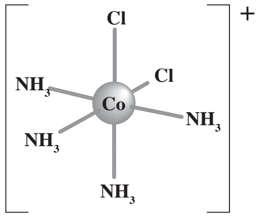


2. A

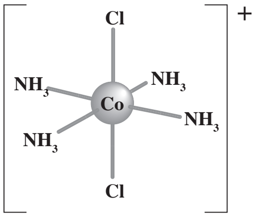
A ligand is an ion or molecule that binds to a central metal atom to form a coordination complex. The bonding with the metal generally involves the contribution of one or more of the ligand's electron pairs to forming the bond(s) to the metal. A ligand is a Lewis base, in other words, an electron pair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

3. C

An octahedral complex such as $[Co(NH_3)_4Cl_2]^+$ 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.



cis



trans

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 (Au^{3+}). The hydrochloric acid provides a ready supply of chloride ions (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 $[Co(NH_3)_6]^{3+}$ is yellow and $[Co(NH_3)_5Cl]^{2+}$ 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 $[Co(NH_3)_6]^{3+}$

8. D

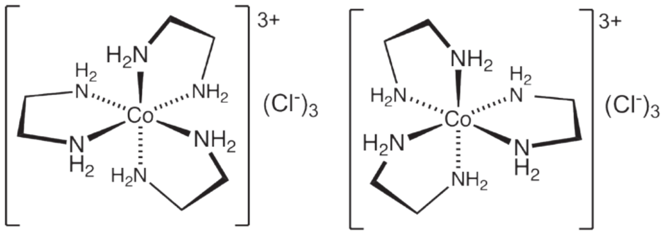
Many transition metal cations actually exist in aqueous solution as a hydrate complex ion. In solution chemistry, we say Cr^{3+}, but the actual form is $[Cr(H_2O)_6]^{3+}$.

The question gives us help in that the answer choices as a whole give us enough to construct the story. Titrating $[Cr(H_2O)_6]^{3+}$ (choice 'A') with base, we are replacing H_2O ligands with OH^- ligands. Eventually we reach $[Cr(H_2O)_3(OH)_3]$ (Compound II, choice 'C'), which is no longer an ion, and so it precipitates. Continuing to titrate with OH^- forms $[Cr(H_2O)_2(OH)_4]^-$ (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.

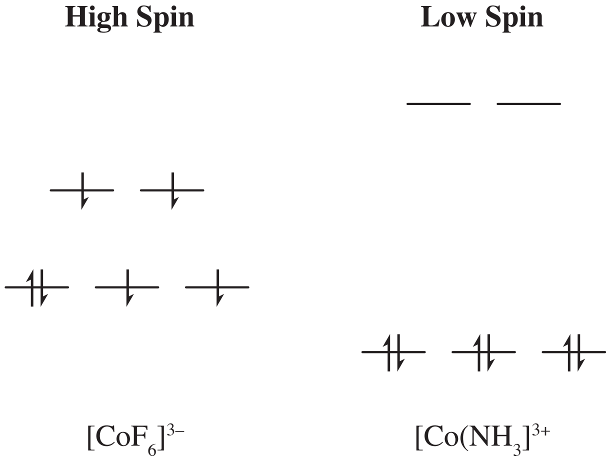
Although this is not an issue for the question, having three bidentate ligands, any tris(ethylenediamine)cobalt(III) complex is not super-imposable on its own mirror image, so there are two enantiomers of the complex.



10. C

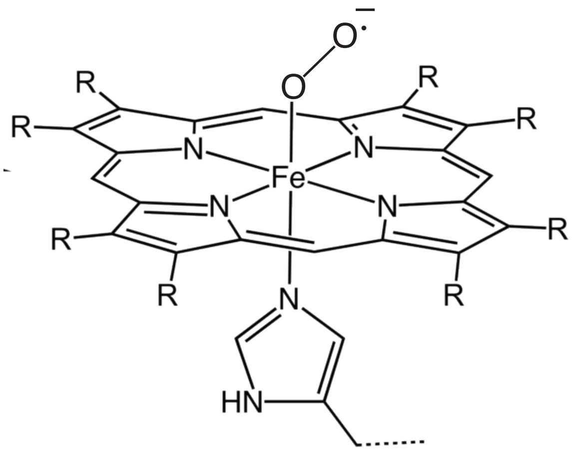
NH_3 is the ligand with the greatest ability to produce a complex with high splitting energy. In a complex with high crystal field splitting energy, the electrons will tend to pair in the lower energy d-subshell orbitals. High splitting energy is consistent with a low spin complex, in other words. If 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).



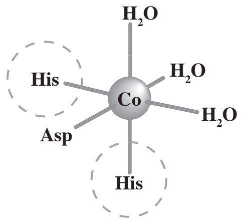
11. C

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.

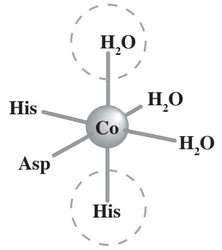


12. B

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.



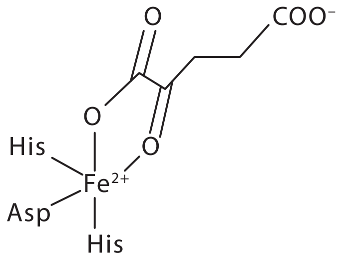
cis



trans

13. B

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



14. A

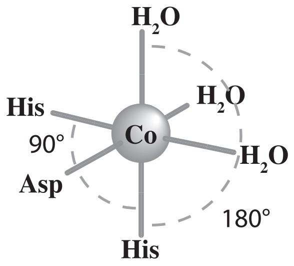
'Ternary complex' is not a term of conceptual vocabulary from coordination chemistry. It's not a kind of coordination complex but a kind of enzyme-substrate complex. A ternary complex is an enzyme-substrate complex formed between two substrate molecules and an enzyme. Multi-substrate enzyme-catalyzed 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 αKG as a coordinating ligand. A Lewis acid is an electron pair receiver.

15. D

Subsequent to decarboxylation of αKG the iron cofactor of an αKG-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.

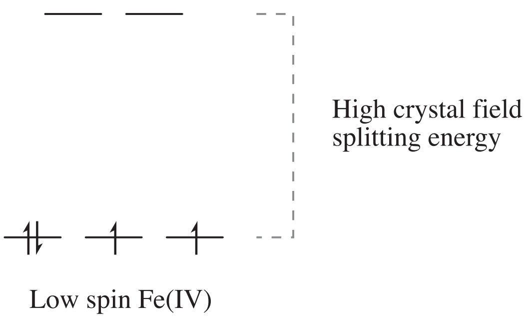
16. B

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



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.