Chapter 23

The Transition Elements

Concept Check 23.1

Another complex studied by Werner has a composition corresponding to the formula $PtCl_4 \cdot 2KCl$. From electrical-conductance measurements, he determined that each formula unit contained three ions. He also found that silver nitrate did not give a precipitate of AgCl with this complex. Write a formula for this complex that agrees with this information.

Solution

Because silver nitrate does not precipitate AgCl from the complex, you conclude that chlorine is not present as free chloride ions; the Cl is presumably present as a complex. Potassium ion is likely present as K^+, which would account for two of the ions present in each formula unit. The other would be a complex ion of platinum with the six chlorine atoms (a complex of Pt with six Cl^- ions). The charge on this complex ion must be -2 to counter the charges from the K^+ ions, so its formula is $PtCl_6^{2-}$. The formula of the complex then is $K_2[PtCl_6]$.

Concept Check 23.2

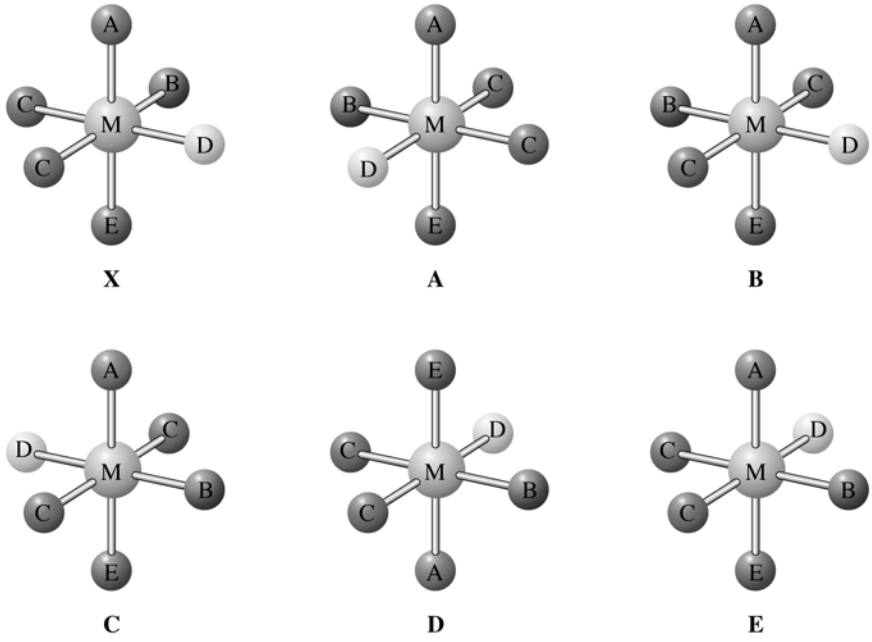
A complex has the composition $Co(NH_3)_4(H_2O)BrCl_2$. Conductance measurements show that there are three ions per formula unit, and precipitation of AgCl with silver nitrate shows that there are two Cl^- ions not coordinated to cobalt. What is the structural formula of the compound? Write the structural formula of an isomer.

Solution

The addition of silver nitrate to the complex precipitates AgCl equivalent to two Cl^- ions per formula unit. Since each formula unit consists of three ions, the complex appears to consist of two Cl^- ions plus a complex ion with a charge of +2. The formula of the complex then would be $[Co(NH_3)_4(H_2O)Br]Cl_2$. The structural formula of a possible constitutional isomer is $[Co(NH_3)_4(H_2O)Cl]BrCl$.

Concept Check 23.3

a. Which of the following molecular models of octahedral complexes are mirror images of the molecule X? Keep in mind that you can rotate the molecules when performing comparisons.
b. Which complexes are optical isomers of molecule X?
c. Identify the distinct geometric isomers of the complex X (Note that some of the models may represent the same molecule).



Solution

a. If you were to place a mirror to the right of the complex X, complex A would directly represent what you would see in the mirror, so it is a mirror image. If you were to place a mirror behind complex X, complex D would also be a mirror image. Note that complexes B and C are exactly the same, and A and E are the same, in both cases, they only differ by rotation (spin one of the complexes in each pair 180° to see this). Therefore, A, D, and E are mirror images.

b. Optical isomers are nonsuperimposable mirror images of one another. The mirror images of molecule X, which are molecules A and D, are both superimposable mirror images, so no optical isomers of X are present.
c. To answer this part, you need to rotate each of the complexes to see if they have the same bonding arrangement in space with each of the ligands. Models A & E are the same complex, neither of which has the same bonding arrangement as complex X, so the complex that they represent is a geometric isomer. Models B & C represent the same complex that also has a different bonding arrangement than complex X, so the complex that they represent is also a geometric isomer. Complex D is the same complex as complex X, so it is not a geometric isomer.

Conceptual Problem 23.27

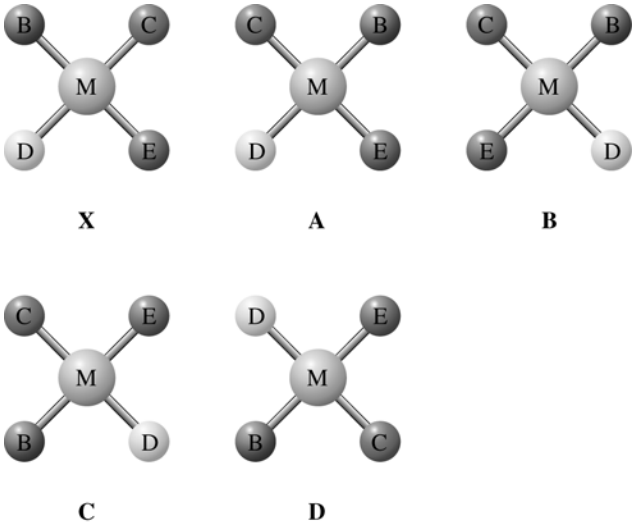
A cobalt complex whose composition corresponded to the formula $Co(NO_2)_2Cl \cdot 4NH_3$ gave an electrical conductance equivalent to two ions per formula unit. Excess silver nitrate solution immediately precipitated 1 mol AgCl per formula unit. Write a structural formula consistent with these results.

Solution

Because one mole of chloride ion is precipitated per formula unit of the complex, the chlorine atoms must be present as chloride ion. All the other ligands are coordinated to the cobalt. An appropriate formula is $[Co(NH_3)_4(NO_2)_2]Cl$.

Conceptual Problem 23.28

For the following coordination compounds, identify the geometric isomer(s) of compound X.



Solution

In order to solve this problem, you need to check each of the possible coordination compounds (A-D) to see if they are different than compound X. Compounds B, C, and D, through rotation and flipping over, all turn out to be the same as compound X. The only compound that is different is A, so it is the only geometric isomer of compound X.

Conceptual Problem 23.29

Describe step by step how the name potassium hexacyanoferrate(II) leads one to the structural formula $K_4[Fe(CN)_6]$.

Solution

"Hexacyano" means that there are six CN^- ligands bonded to the iron cation. The Roman numeral II means that the oxidation state of the iron cation is +2, so that the overall charge of the complex ion is -4. This requires four potassium ions to counterbalance the -4 charge.

Conceptual Problem 23.30

Compounds A and B are known to be stereoisomers of one another. Compound A has a violet color; compound B has a green color. Are they geometric or optical isomers?

Solution

Compounds A and B are geometric isomers because these isomers have different physical properties whereas optical isomers do not.

Conceptual Problem 23.31

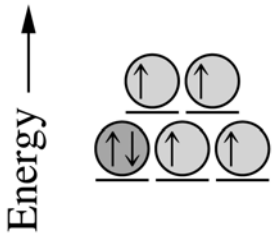
A complex has a composition corresponding to the formula $CoBr_2Cl{\cdot}4NH_3$. What is the structural formula if conductance measurements show two ions per formula unit? Silver nitrate solution gives an immediate precipitate of AgCl but no AgBr. Write the structural formula of an isomer.

Solution

The given compound must consist of a chloride ion (which can be precipitated with $AgNO_3$ solution) and a $[Co(NH_3)_4Br_2]^+$ ion, giving $[Co(NH_3)_4Br_2]Cl$. The structural formula of a possible constitutional isomer is $[Co(NH_3)_4BrCl]Br$.

Conceptual Problem 23.32

For the complexes shown here, which complex anion would have the *d* electron distribution shown in the diagram below: MF_6^{3-}, $M(CN)_6^{3-}$, MF_6^{4-}, $M(CN)_6^{4-}$? Note that the neutral metal atom, M, in each complex is the same and has the ground state electron configuration $[Ar]4s^2 3d^6$.



Solution

The *d* orbital energy level diagram contains six electrons. This indicates that the metal M must have the electron configuration $[Ar]3d^6$ and therefore a charge of 2+ (M^{2+}). The two complexes that have M in the 2+ oxidation state are MF_6^{4-} and $M(CN)_6^{4-}$. The *d* orbital energy level diagram is high spin indicating that there is a relatively small amount of crystal field splitting. According to the spectrochemical series, F^- is a less strongly bonding ligand with a relatively smaller crystal field splitting, which makes the MF_6^{4-} the most likely answer.