

## Chapter 3

### Structures of Coordination Compounds

#### Problem Solutions:

3.1. Ethanol and dimethylether are isomers because they have the same number and types of atoms but different properties. Furthermore, they are structural isomers because they have different numbers and types of chemical bonds. For example, ethanol has one C-O bond while dimethylether has two.

3.2. The three different forms of a chaise lounge are more like stereoisomers because they have the same number and types of "chemical bonds" but differ in the spatial arrangements of those "bonds."

3.3. The two chain theory formulations would be considered to be stereoisomers because they have the same numbers and types of chemical bonds (three each of Co-N,  $\text{NH}_3\text{-NH}_3$ , and  $\text{NH}_3\text{-Cl}$ ) but differ in the spatial arrangements of those bonds.

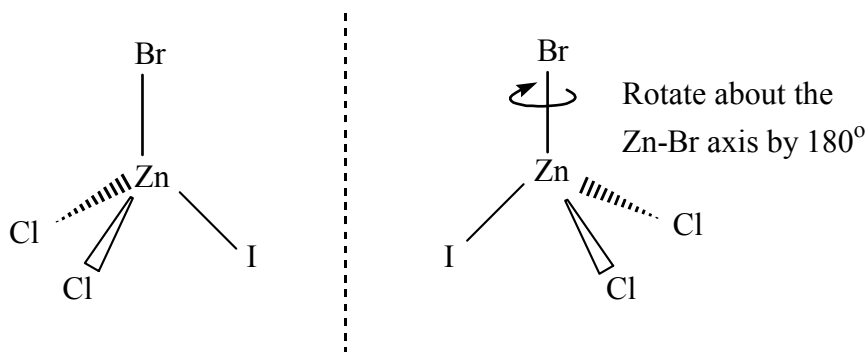
3.4. These are stereoisomers. Each has the same numbers and types of chemical bonds but differ in the spatial arrangements of those bonds.

3.5. A light beam of a given wavelength can be polarized such that only one plane of the electric or magnetic field is allowed. A molecule is optically active if it is capable of rotating that plane to the right or to the left when the light beam is passed through the substance.

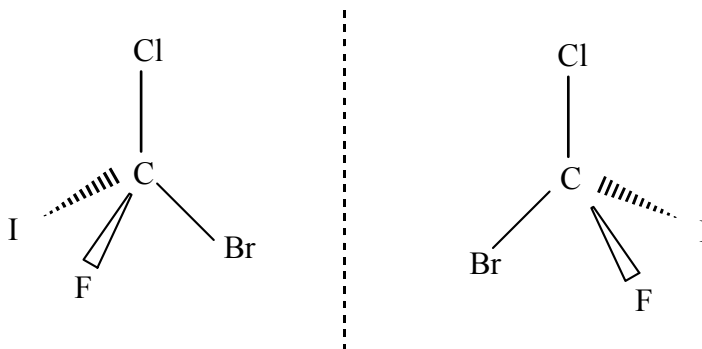
3.6. Each of these sets of isomers (the 1,2; 1,3; and 1,4 for the  $\text{MA}_4\text{B}_2$  and the 1,2,3; 1,2,4; and 1,3,5 for the  $\text{MA}_3\text{B}_3$ ) are geometric isomers because their different spatial arrangements result in different geometries. None of these geometric isomers are chiral because each contains at least one internal mirror plane, namely that of the hexagon itself.

\*3.7. For each case ( $\text{MA}_4\text{B}_2$  and  $\text{MA}_3\text{B}_3$ ), these are geometric isomers because they have the same numbers and types of chemical bonds but the different spatial arrangements of these bonds result in different geometries. In the  $\text{MA}_4\text{B}_2$  set the 1,6 case does not contain an internal mirror plane and is chiral. The 1,5 isomer is actually the nonsuperimposable mirror image of the 1,6 isomer. Similarly, in the  $\text{MA}_3\text{B}_3$  the 1,2,4 isomer is chiral. The 1,2,5 isomer is its nonsuperimposable mirror image.

3.8. The two mirror images of bromodichloroiodozincate(II), shown below, can be superimposed upon each other by rotating one isomer  $180^\circ$  about the Zn-Br axis. Therefore, this molecule is not chiral. The same conclusion is arrived at by considering that the molecule has at least one internal mirror plane.



3.9. These two mirror images are nonsuperimposable. No matter how one is rotated in space, it cannot be made equivalent to the other. Therefore, this molecule is chiral. The same conclusion is arrived at by considering the fact that this molecule does not contain any internal mirror planes.

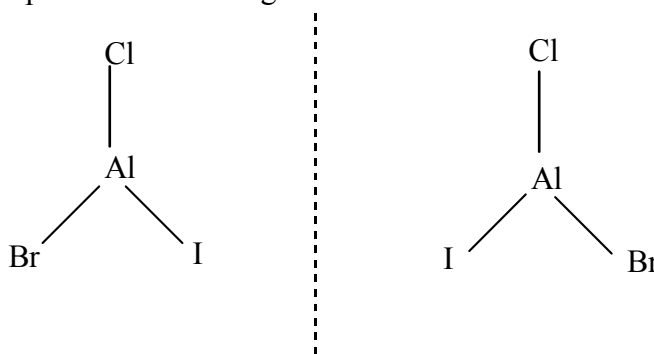


3.10. In a molecule of formula  $Mabcd$ , only a tetrahedral structure will be chiral. It will have no internal mirror planes. In the square planar molecule, the plane of the square is an internal mirror plane. Therefore the square planar  $Mabcd$  is not chiral.

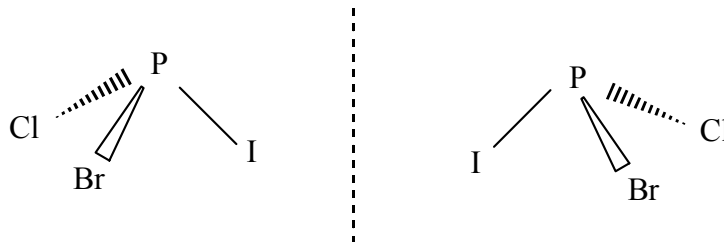
3.11. (a) If the mirror image of a molecule cannot be rotated in space so as to be equivalent to the original molecule, it is said to have a nonsuperimposable mirror image. Such a molecule is chiral. (b) If a molecule does not possess an internal mirror plane (a plane that passes through the molecule such that every atom in the molecule can be reflected through the plane into another equivalent atom) it is chiral. [There are a few exceptions to this rule but they are beyond the scope of this text.]

\*3.12. Only  $PClBrI$  is chiral because it has a nonsuperimposable mirror image.

The mirror image is superimposable on the original molecule. To see this, picture the mirror image rotated  $180^\circ$  about the  $Al-Cl$  axis.

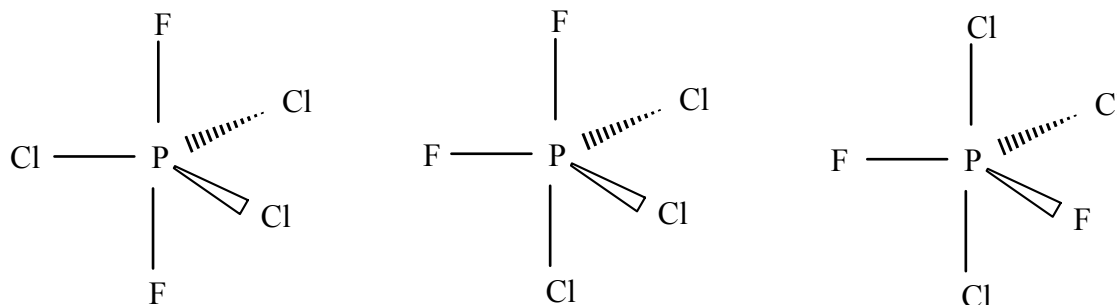


Here, the mirror image cannot be superimposed on the original molecule.



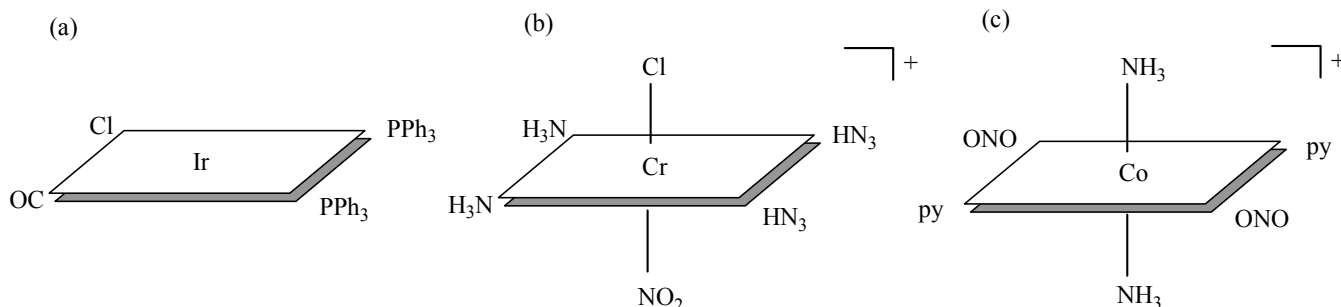
3.13. Only  $AlClBrI$  has an internal mirror plane, the one that the entire molecule sits in. Therefore, this molecule is not chiral whereas the corresponding phosphorus compound is.

3.14. There are three possible isomers of  $\text{PF}_2\text{Cl}_3$  as shown below. Each of these possesses at least one internal mirror plane. Therefore, none of these isomers is chiral.

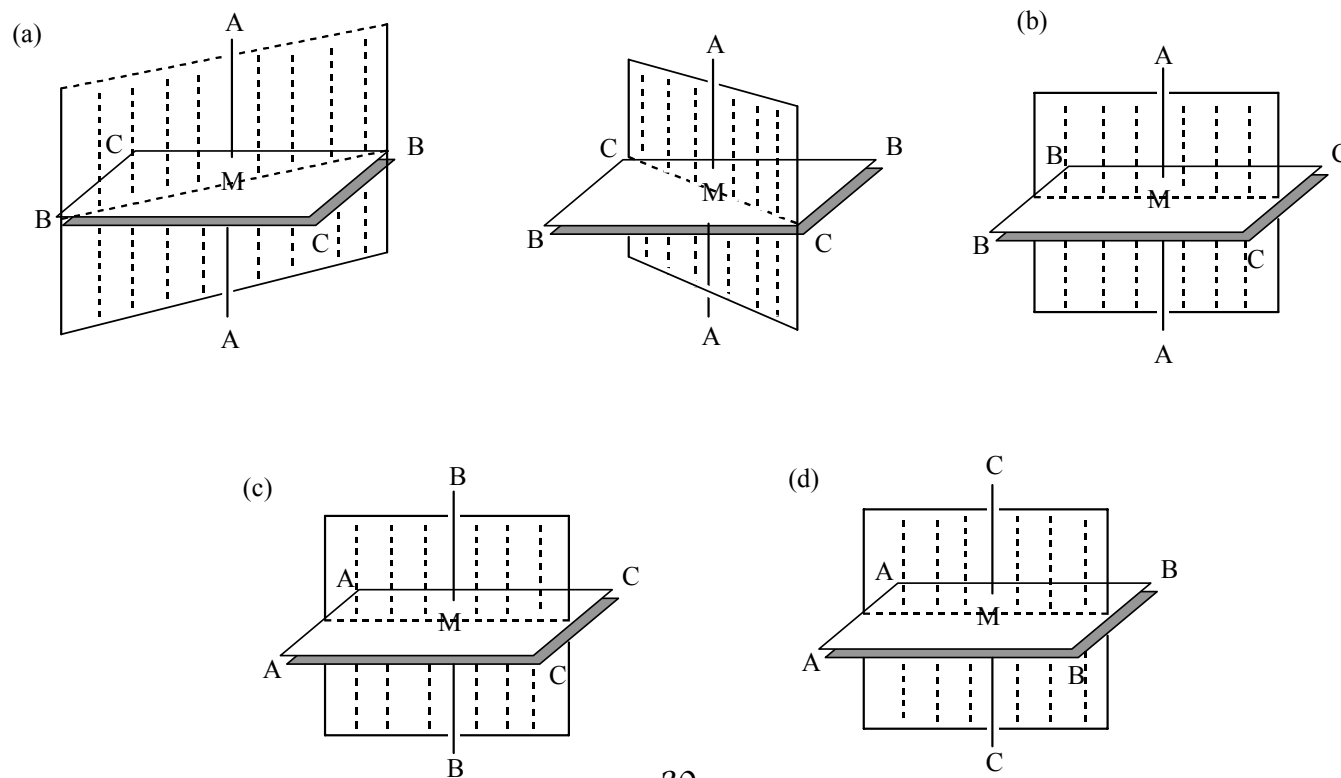


[Note: For the purposes of considering the chirality of the above three forms, we are assuming that the above molecules are nonfluxional.]

3.15. The structural formulas are as follows: (For (b) and (c), the structure of only the cations are shown.)

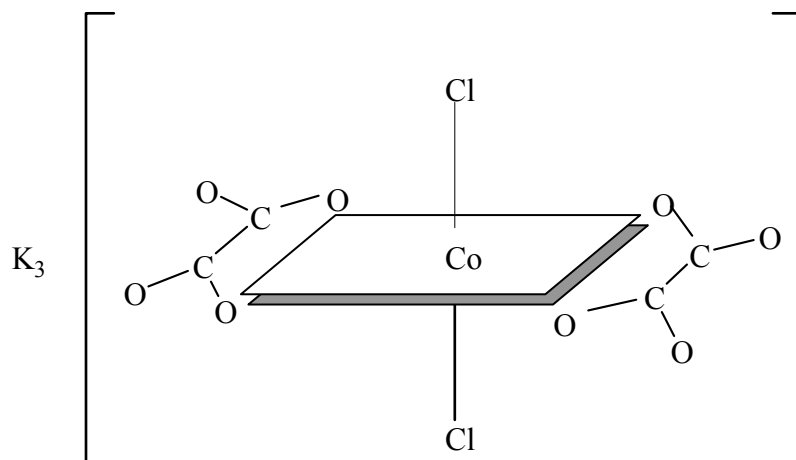


3.16. There are two additional internal mirror planes in (a) and one additional in (b), (c), and (d). These are shown below.

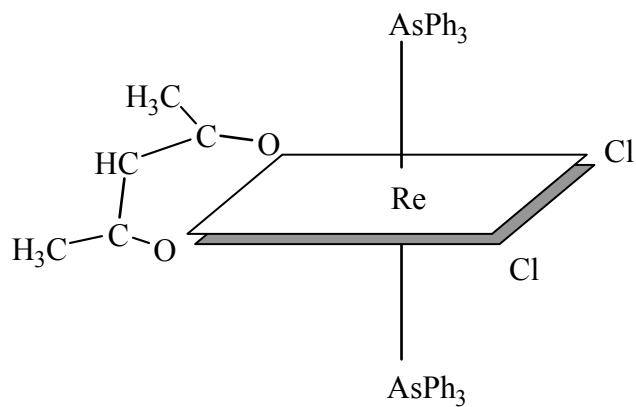


3.17. Neither of these compounds is chiral because each contains at least one internal mirror plane.

(a)

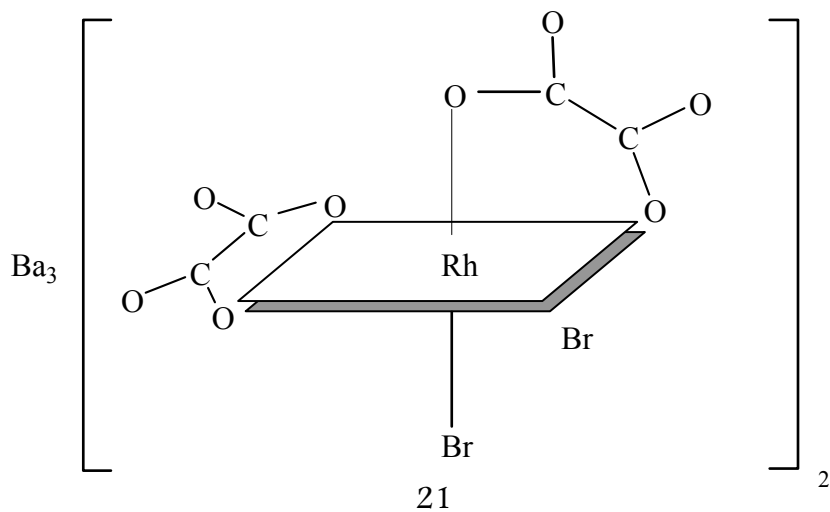


(b)

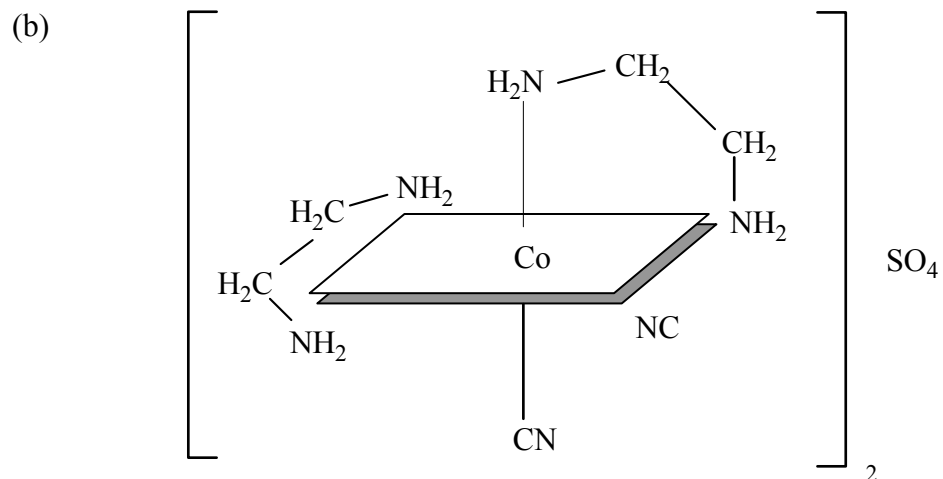


3.18 Both of the complex ions are chiral because they lack an internal plane of symmetry.

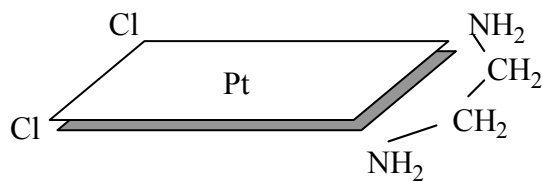
(a)



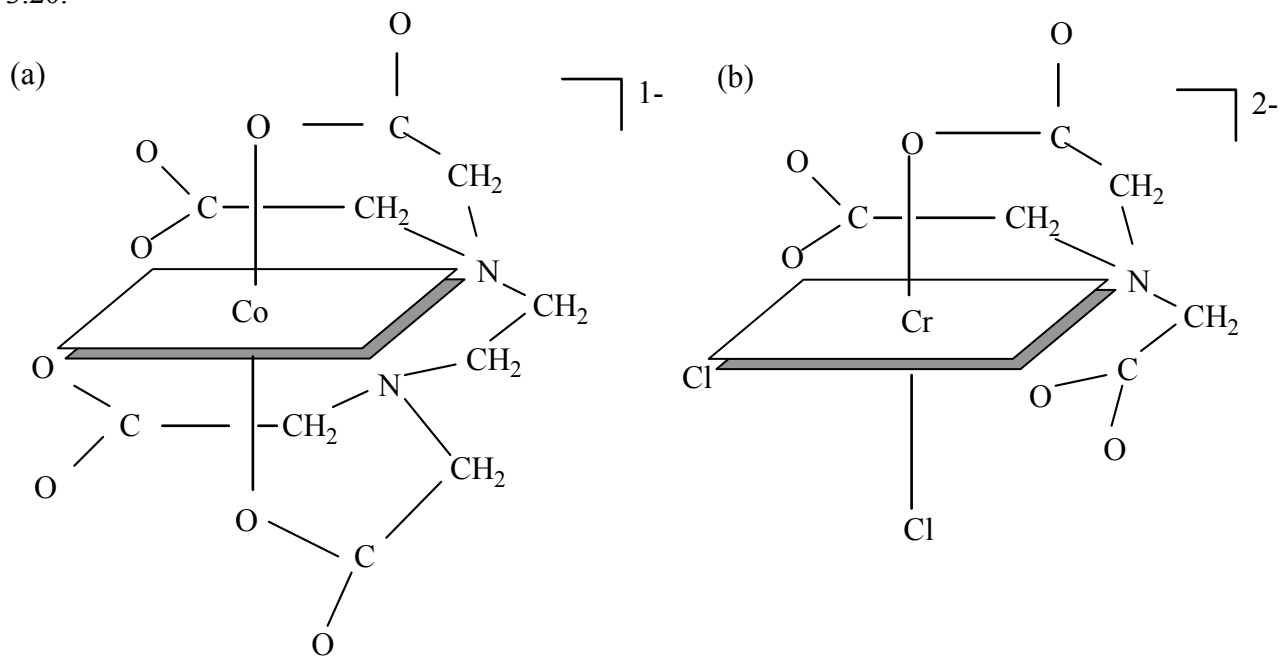
3.18



- 3.19 (a)  $[\text{Cr}(\text{C}_2\text{O}_4)_3]$  chiral due to propeller shape with no internal mirror planes  
 (b) Not chiral due to several internal mirror planes including the plane of the molecule.



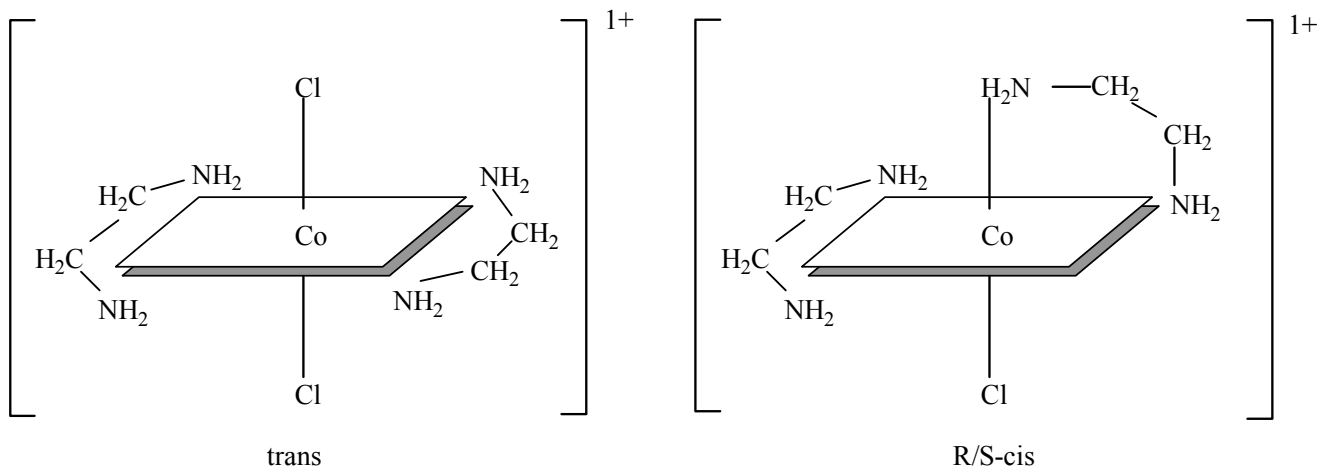
3.20.



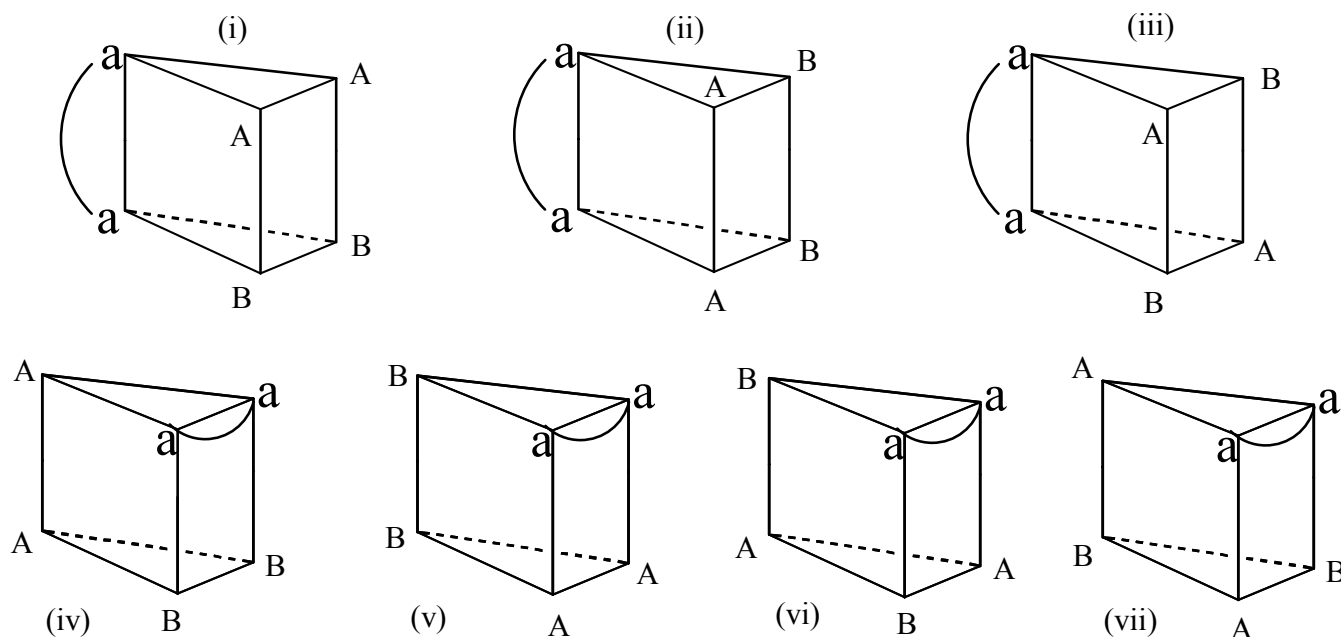
The EDTA complex does not contain an internal mirror plane and is chiral. The NTA complex always contains such a plane and is not chiral.

\*3.21. Prior to Werner's synthesis and resolution of coordination compounds containing chelating agents, the evidence for his coordination theory had been "negative." That is to say, his theory often predicted only two isomers for a given  $MA_4B_2$  or  $MA_3B_3$  complex (where A and B are monodentate ligands) if the geometry of the coordination sphere was octahedral. Planar hexagonal and trigonal prismatic geometries, on the other hand, yielded three isomers in each case. His and other research groups indeed could synthesize only two isomers of these compounds. But what if the correct geometry was hexagonal or trigonal prismatic and the third isomer was just particularly difficult to synthesize? Werner had only "negative" evidence for his octahedral coordination theory. It was the *absence* of a given isomer that Werner claimed supported his ideas. However, octahedral coordination spheres for a complex of general formula  $M(AA)_2B_2$  (where AA = a chelating bidentate ligand) should have one chiral and one nonchiral form. Werner and his group were able to confirm the existence of this number of isomers and therefore provide "positive" evidence for his theory and the octahedral configuration of his secondary valence.

3.22. cis- and trans-dichlorobis(ethylenediamine)cobalt (III) chloride. The cation is shown in each case.

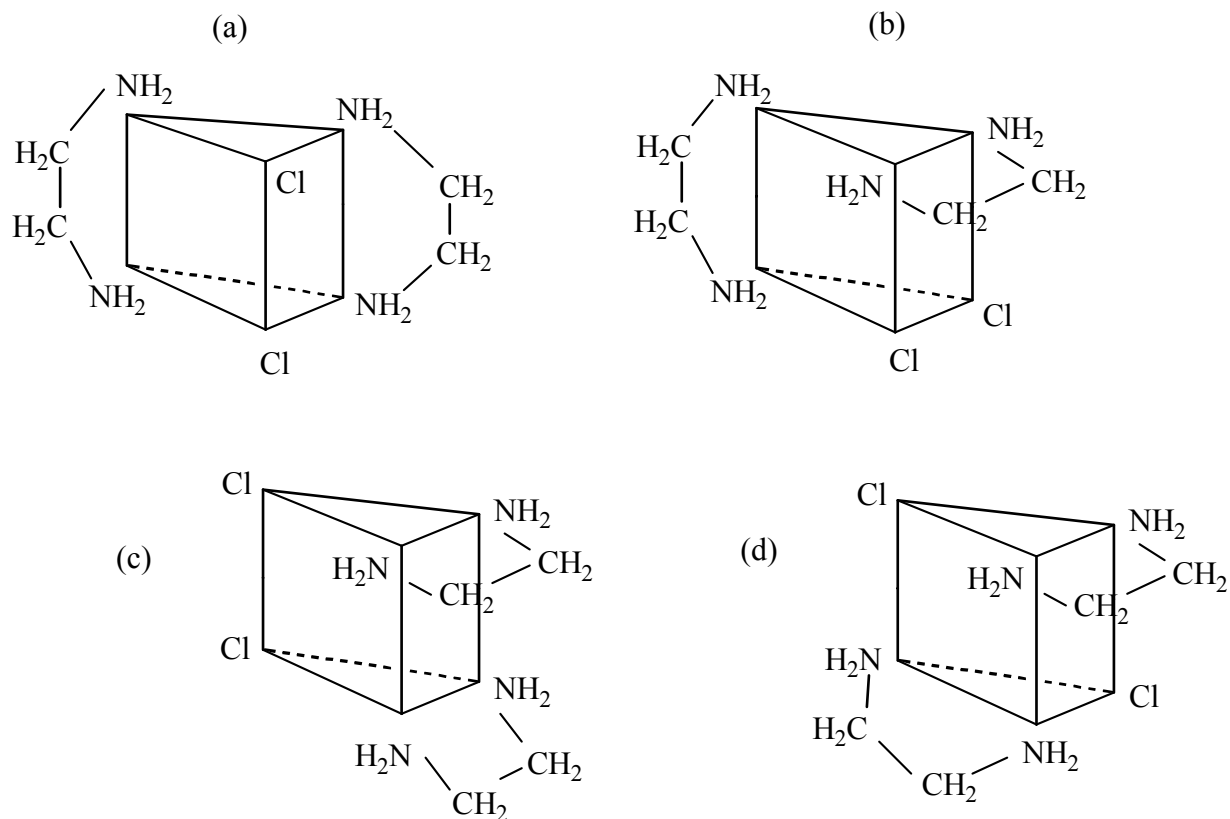


\*3.23. Structures (iii), (vi) and (vii) are chiral as they lack an internal mirror plane.

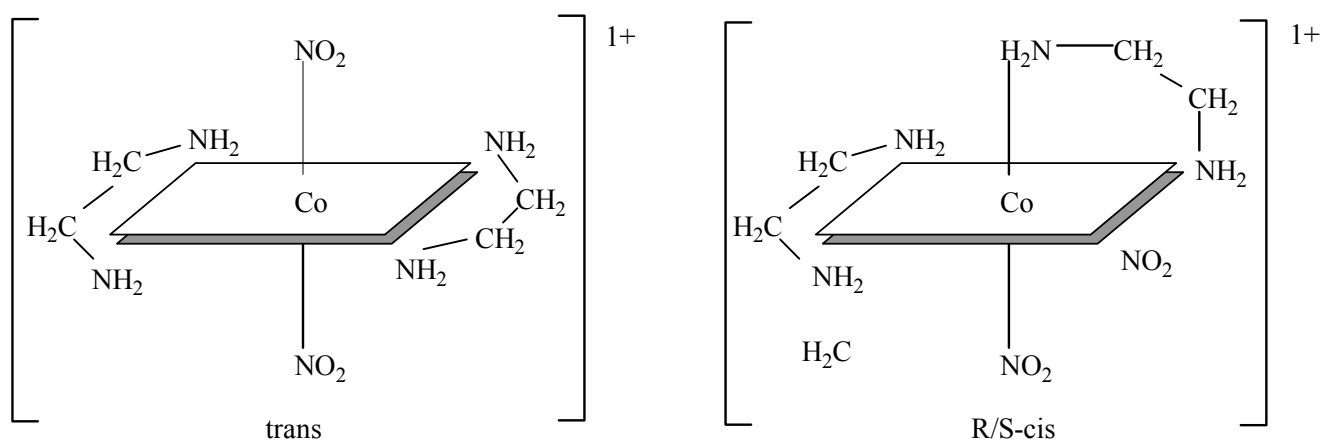




\*3.24. For the complex cation of this compound (shown without its charge), there would be four possible geometric isomers as shown below. Only the last, (d), lacks an internal mirror plane and is chiral.

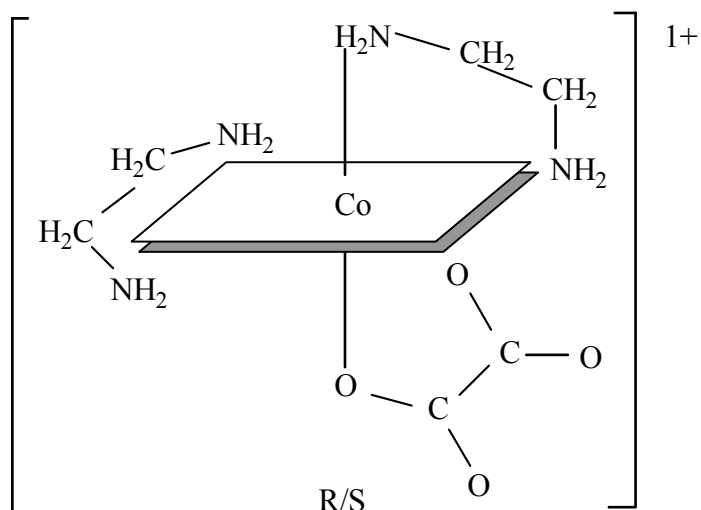


3.25.



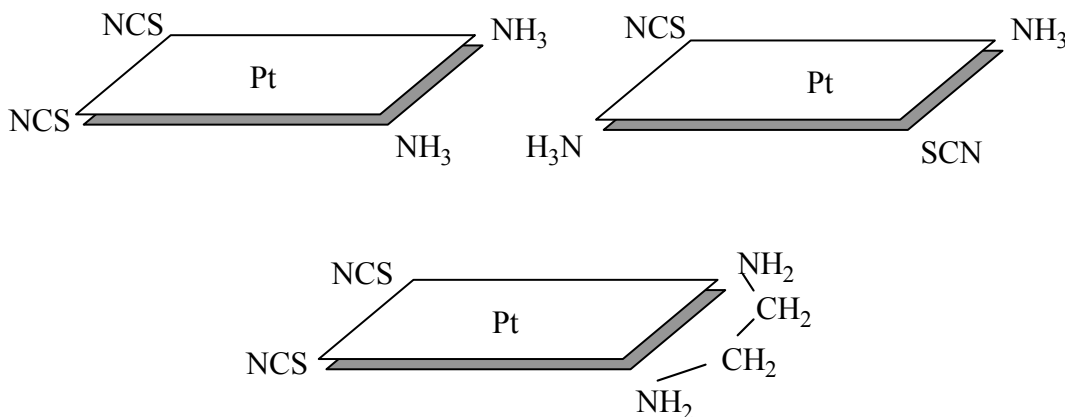
3.26. Since both the ethylenediamine and oxalate ligands can only span the cis positions of an octahedron, there is only one possible geometric isomer for this complex. This cation (shown below without its +1 charge) lacks a plane of symmetry and is chiral.





3.27. No, the structure would then have a plane of symmetry and would no longer be chiral. The plane of symmetry would contain the C-C bond of the methyl-substituted ethylenediamine, pass through the platinum cation, and then bisect the C-C bond of the phenyl ( $\text{C}_6\text{H}_5$ ) - substituted ethylenediamine.

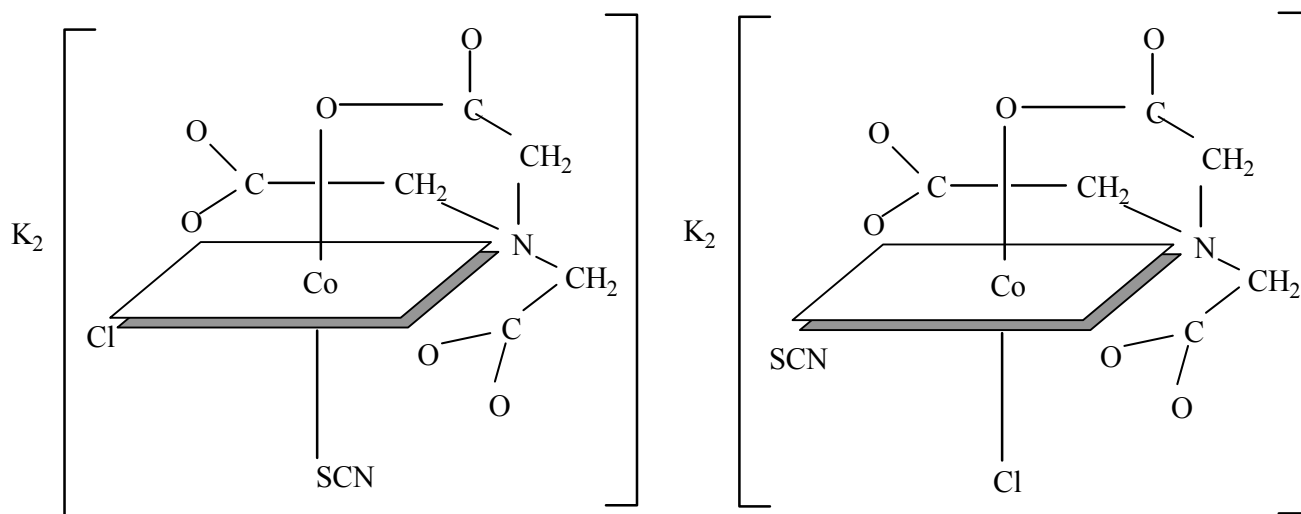
3.28.



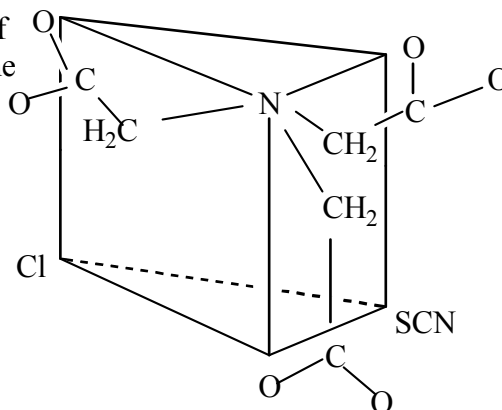
It proves that the coordination sphere about the platinum(II) cation is square planar. Cis- and trans- isomers are not possible in a tetrahedral configuration. If these complexes were tetrahedral, only one isomer would be possible in each case. Square planar complexes give the opportunity for cis and trans forms as long as there are monodentate ligands involved. The bidentate ethylenediamine, however, can only span cis positions so there is only one isomer in that case.

3.29. (a) potassium chloro(nitritotriacetato)thiocyanatocobaltate(III)

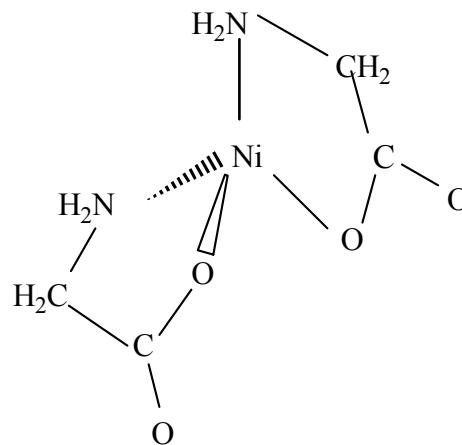
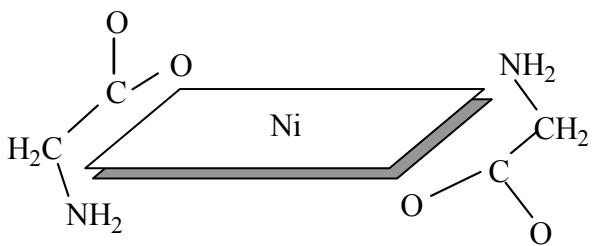
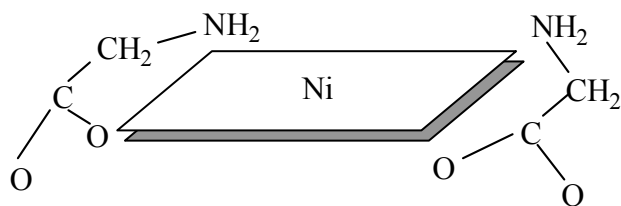
(b) Since the four binding sites of the NTA must be adjacent to each other, the two monodentate ligands ( $\text{SCN}^-$  and  $\text{Cl}^-$ ) also must always be cis to each other. However, either the chloride or the thiocyanate could be trans to the nitrogen of the NTA as shown below. In either case, the complex anion contains an internal mirror plane and is therefore not chiral.



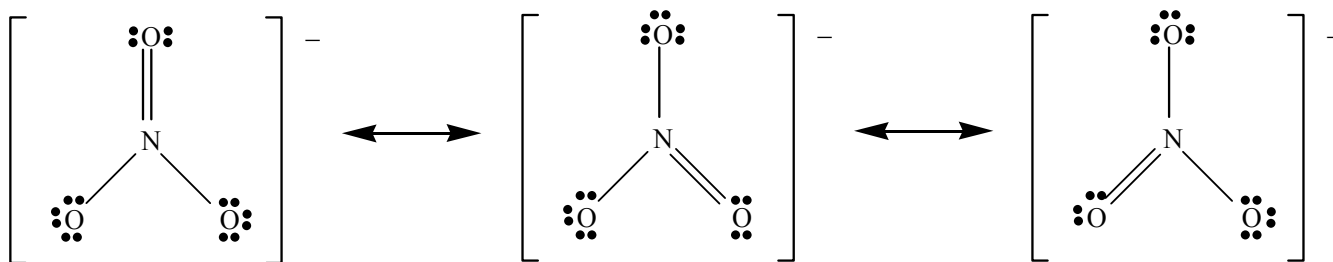
\*3.30. If the coordination sphere were trigonal prismatic instead of octahedral, the resulting complex anion would have only one possible geometric isomer. This structure, however, would not possess an internal plane of symmetry and would be chiral.



\*3.31. Both of the square planar structures possess a plane of symmetry (the plane of the molecule), but the one tetrahedral structure does not. Therefore the square planar versions are nonchiral while the tetrahedral is chiral.



3.32. (a) Since this ligand can only bind to a metal center through an oxygen atom, it cannot be ambidentate.

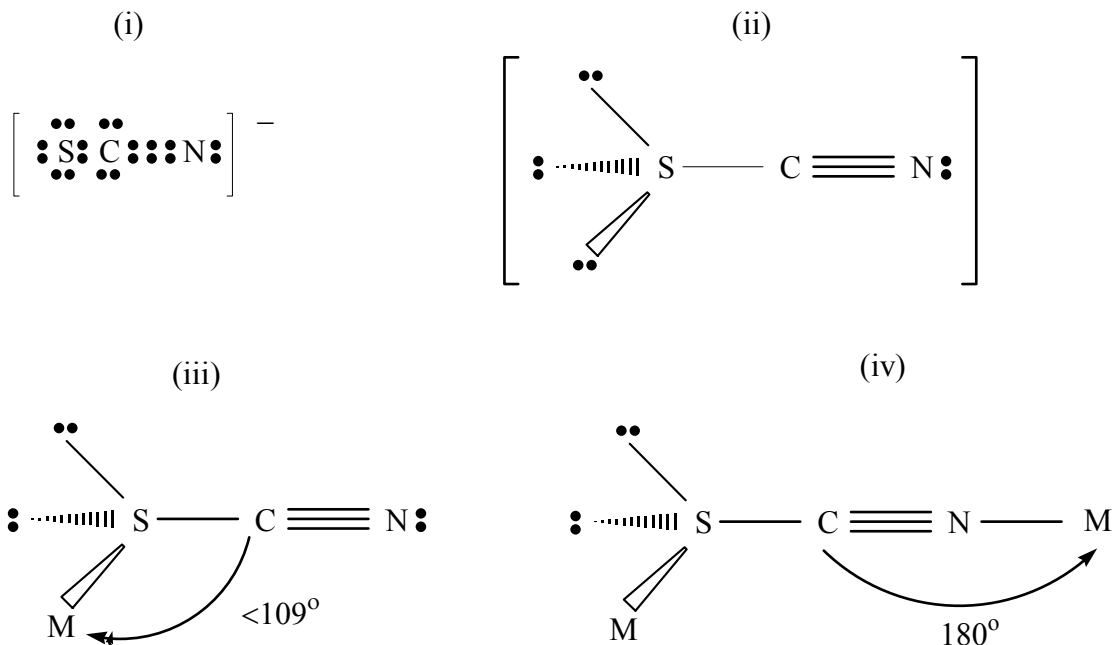


(b) Since compounds containing six  $\text{Co}^{3+}$ -N interactions were always yellow whereas those containing five  $\text{Co}^{3+}$ -N and one  $\text{Co}^{3+}$ -O interactions were red, Werner and Jørgensen were able to confirm the structure of this red compound. Today, we know that this compound must have one  $\text{Co}^{3+}$ -O bond because the nitrate ion does not have a lone pair of electrons on a nitrogen atom.

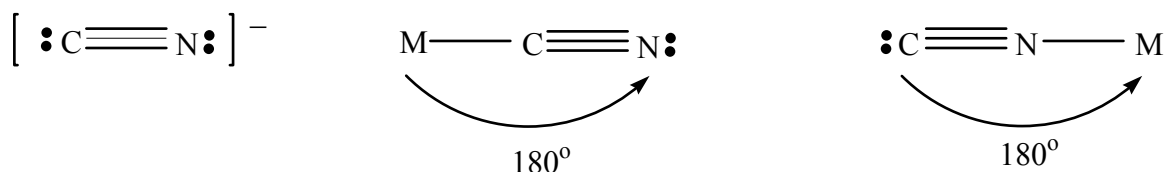
\*3.33. Since the nitrate ligand is capable only of O-bonding to a metal center, both the bis(ethylenediamine)dinitratocobalt(III) chloride and the bis(ethylenediamine)dinitritocobalt(III) chloride possess four  $\text{Co}^{3+}$ -N and two  $\text{Co}^{3+}$ -O interactions. Therefore it follows that both of these compounds should be the same color while the bis(ethylenediamine)dinitrocobalt(III) chloride, in which the complex cation contains six  $\text{Co}^{3+}$ -N interactions, should be a different color.

3.34. (a)  $[\text{Co}(\text{en})_2(\text{NO}_2)_2][\text{AuCl}_4]$ , bis(ethylenediamine)dinitrocobalt(III) tetrachloroaurate(III)  
 (b)  $[\text{Co}(\text{en})_2(\text{ONO})_2][\text{AuCl}_4]$ , bis(ethylenediamine)dinitritocobalt(III) tetrachloroaurate(III)

\*3.35. The Lewis and VSEPR structures of thiocyanate are shown in (i) and (ii) below. The sulfur has three lone pairs available to bind with a metal center while the nitrogen has only one. Assuming the four electron pairs around the sulfur (three lone pairs and one bonding pair) are tetrahedrally dispersed, S-bonded  $\text{SCN}^-$  complexes should possess a nonlinear M-S-C interaction. Given the linear arrangement of the triple bond and the one lone pair about the nitrogen atom, on the other hand (or is it on the other tooth?) N-bonded thiocyanate complexes should possess a linear M-N-C interaction. These two cases are shown in structures (iii) and (iv), respectively.



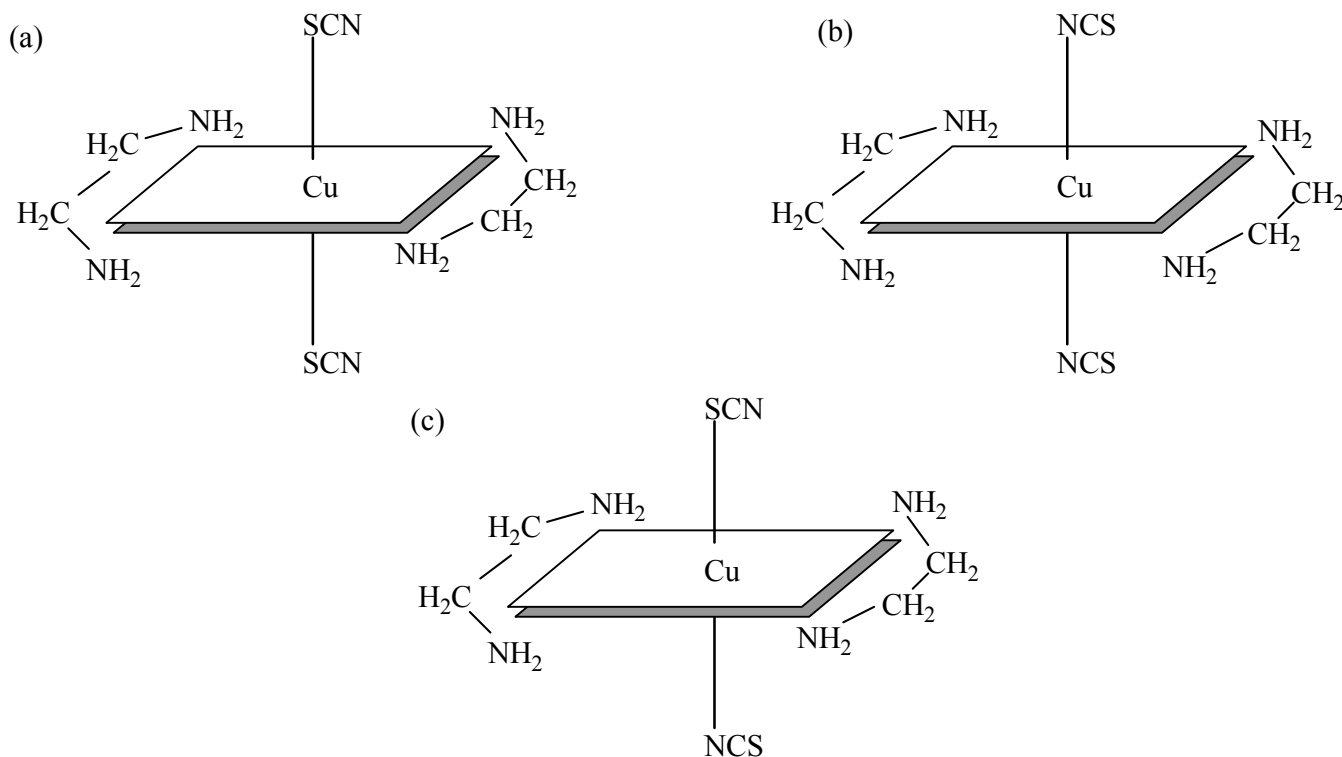
3.36. Given the fact that both the carbon and nitrogen ends of the cyanide ion have a linear arrangement of the triple bond and the lone pair, we would expect both the cyano and isocyano forms to form linear bonds with a metal center.



\*3.37. S-bonded thiocyanate will take up more space around a metal atom or ion because the -SCN is able to rotate about the M-S bond and sweep out a fairly large cone-shaped volume. N-bonded thiocyanate, on the other hand (tooth?) rotates about the M-N bond and sweeps out a much smaller, needle-like cylindrical volume. In the  $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$  cation, the five ammonia ligands sweep out cone-like volumes and take up a fair amount of volume. They do not leave much volume available for the thiocyanate so it is more stable in the isothiocyanate "needle" form that does not require as much volume. In the  $[\text{Co}(\text{CN})_5\text{SCN}]^{3-}$  anion, the linear CN<sup>-</sup> ligands take up very little volume and so the S-bonded SCN<sup>-</sup>, that takes up more space, is favored.

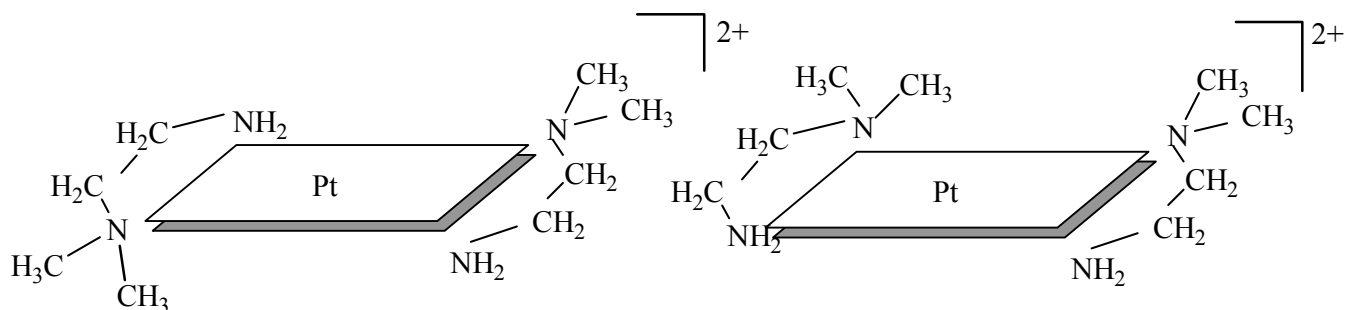
3.38. The three possible linkage isomers are as follows:

- trans-bis(ethylenediamine)dithiocyanatocopper(II)
- trans-bis(ethylenediamine)diisothiocyanatocopper(II)
- trans-bis(ethylenediamine)isothiocyanatothiocyancopper(II)



- 3.39.  $[\text{Cu}(\text{NH}_3)_4][\text{PtBr}_4]$ , tetraamminecopper(II) tetrabromoplatinate(II)  
 $[\text{Cu}(\text{NH}_3)_3\text{Br}][\text{Pt}(\text{NH}_3)\text{Br}_3]$ , triamminebromocopper(II) amminetribromoplatinate(II)  
 $[\text{Pt}(\text{NH}_3)_3\text{Br}][\text{Cu}(\text{NH}_3)\text{Br}_3]$ , triamminebromoplatinum(II) amminetribromocuprate(II)  
 $[\text{Pt}(\text{NH}_3)_4][\text{CuBr}_4]$ , tetraammineplatinum(II) tetrabromocuprate(II)

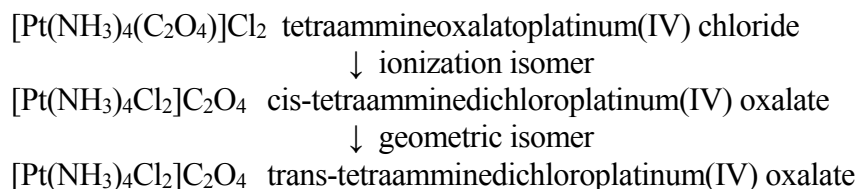
\*3.40. cis- and trans-bis(N,N-dimethylethylenediamine)platinum chloride (only the cations are shown).



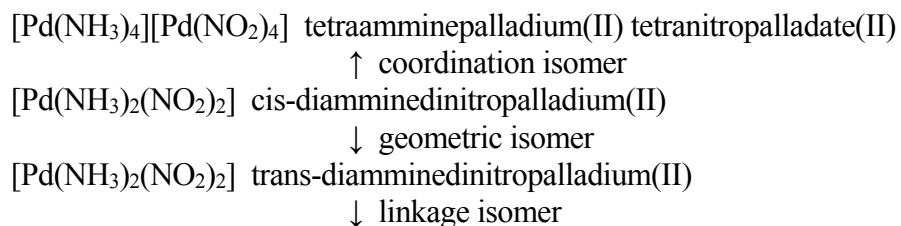
\*3.41. Since all four positions in a tetrahedral are adjacent to each other, there would only one possible geometric isomer for  $[\text{M}(\text{dmen})_2]$ . This isomer would be chiral because it would lack an internal mirror plane.

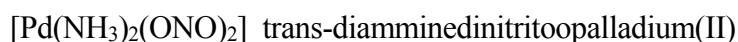
- 3.42. (a)  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]\text{SO}_4$ : An ionization isomer would be  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$ , pentaammine-sulfatocobalt(III) nitrate.  
 (b)  $[\text{Cr}(\text{en})_3][\text{Cr}(\text{C}_2\text{O}_4)_3]$ : A coordination isomer would be  $[\text{Cr}(\text{en})_2(\text{C}_2\text{O}_4)][\text{Cr}(\text{C}_2\text{O}_4)_2(\text{en})]$ , bis(ethylenediamine)oxalatochromium(III) (ethylenediamine)dioxalatochromate(III).
- 3.43. (a)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$ : An ionization isomer would be  $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$ , dibromotetraammine-platinum(IV) chloride.  
 (b)  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ : A coordination isomer would be  $[\text{Cu}(\text{NH}_3)_3\text{Cl}][\text{Pt}(\text{NH}_3)\text{Cl}_3]$ , triamminechlorocopper(II) amminetrichloroplatinate(II).

\*3.44. The following ionization and geometric isomers are possible. However, no optical, coordination, or linkage isomers are possible.



\*3.45. At least one of each type of isomer except optical is possible as shown below.





\*3.46. All five types of isomers can be illustrated as shown below.

