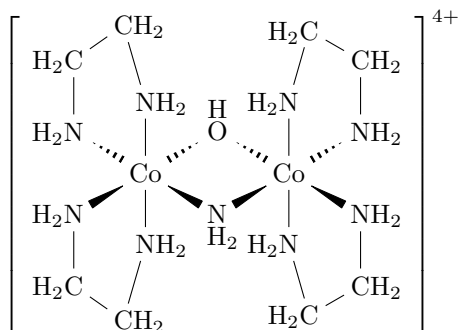


2/19: I) Do the following problems from Chapter 9: 7; 9; 12a,b,e; 20; 23.

9.7 Give structures for the following:

a. Bis(en)Co(III)- μ -amido- μ -hydroxobis(en)Co(III) ion.

Answer.

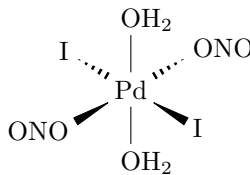


□

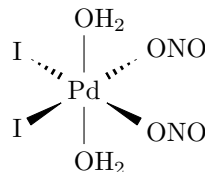
b. DiaquadiiododinitritoPd(IV), all isomers.

Answer. There are six stereoisomers of diaquadiiododinitritoPd(IV). We will classify them into five groups by the relative positions of like ligands as follows. One group will contain two enantiomers.

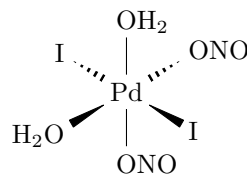
1. All like ligands *trans*.



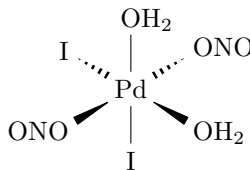
2. *trans*-aqua, *cis*-everything else.



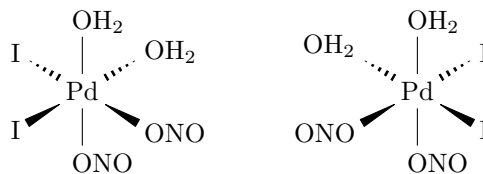
3. *trans*-iodo, *cis*-everything else.



4. *trans*-nitrito, *cis*-everything else.

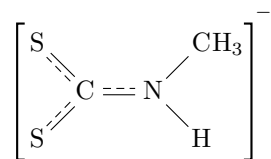


5. All like ligands *cis*.



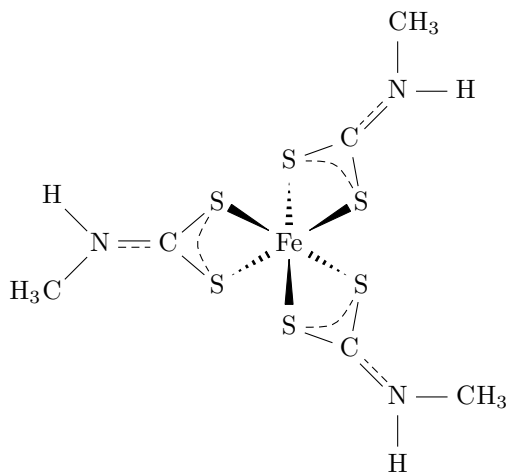
□

c. $\text{Fe}(\text{dtc})_3$, all isomers, where dtc is

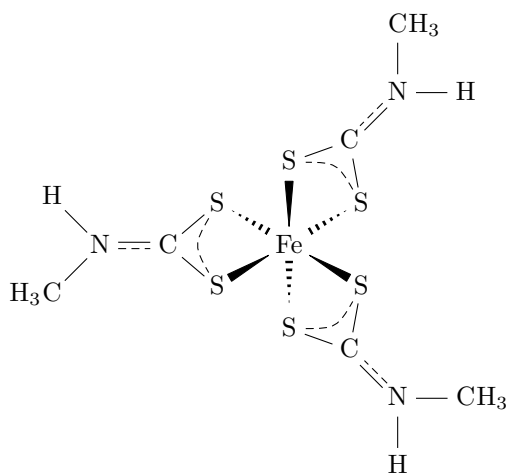


Answer. There are two stereoisomers of $\text{Fe}(\text{dtc})_3$ if we consider the bidentate ligand to be a simple bridge: one Λ form and one Δ form.

1. Λ form.



2. Δ form.

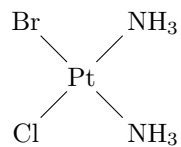


□

9.9 Show structures for the following:

a. *cis*-Diamminebromochloroplatinum(II).

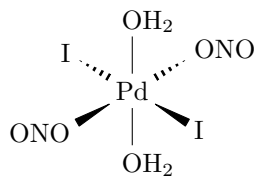
Answer.



□

b. Diaquadiiododinitritopalladium(IV), all ligands *trans*.

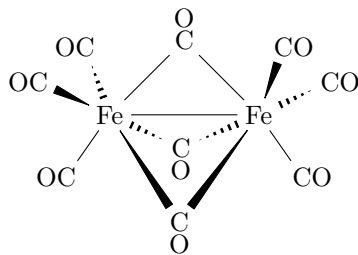
Answer.



□

c. Tri- μ -carbonylbis(tricarbonyliron(0)).

Answer.

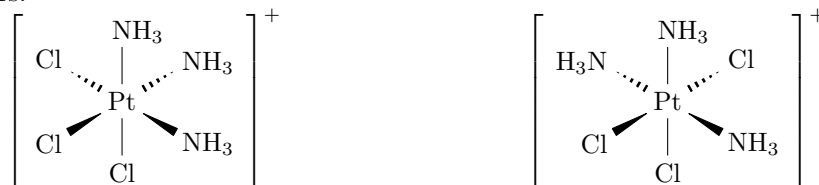


□

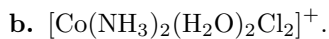
9.12 Sketch all isomers of the following. Indicate clearly each pair of enantiomers.



Answer. There is one facial and one meridional isomer of $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]^+$. There are no enantiomers.

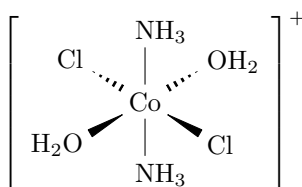


□

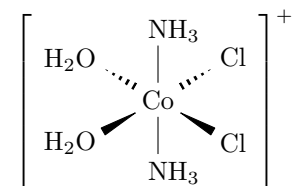


Answer.

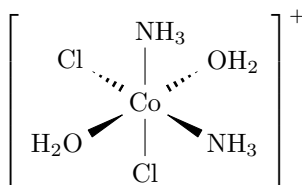
1. All like ligands *trans*.



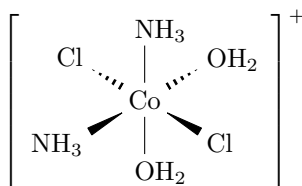
2. *trans*-ammine, *cis*-everything else.



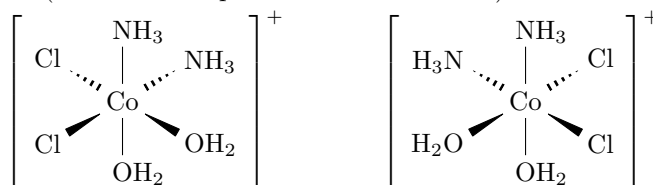
3. *trans*-aqua, *cis*-everything else.



4. *trans*-chloro, *cis*-everything else.



5. All like ligands *cis* (these two compounds are enantiomers).

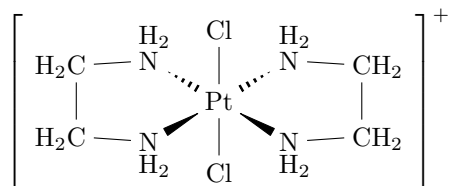


□

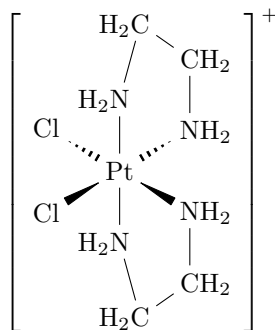
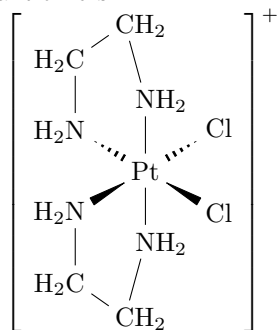
e. $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$.

Answer. There is one achiral isomer and one pair of chiral enantiomers.

1. Achiral isomer.

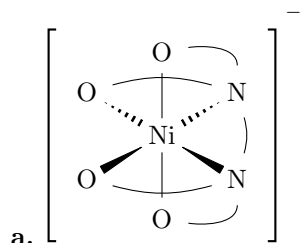


2. Chiral enantiomers.

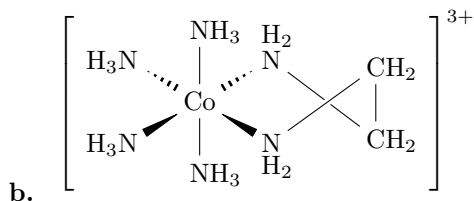


□

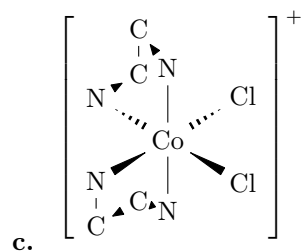
9.20 Which of the following molecules are chiral?



Answer. This molecule is chiral. □



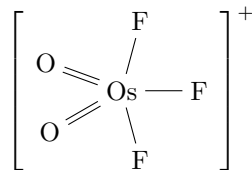
Answer. This molecule is achiral (if we assume that the ring on the right side largely lies in the plane with quickly reversing buckling or puckering, a reasonable hypothesis given the light N and C atoms). It is chiral if we assume a rigid ring in the pictured conformation. □



Answer. This molecule is chiral. □

- 9.23** When *cis*-OsO₂F₄ is dissolved in SbF₅, the cation OsO₂F₃⁺ is formed. The ¹⁹F NMR spectrum of this cation shows two resonances, a doublet and a triplet having relative intensities of 2 : 1. What is the most likely structure of this ion? What is its point group? (See Casteel et al., 1996.)

Answer. From Bent's rule and sterics, we would predict the following structure, which has point group C_{2v} .



Moreover, this structure is supported by the ¹⁹F NMR data, since we have two equivalent (axial) fluorines on the same central atom as one nonequivalent fluorine (causing a doublet by the $n + 1$ rule of relative intensity 2) and, reversing roles, one (equatorial) fluorine on the same central atom as two separate but equivalent fluorines (causing a triplet by the $n + 1$ rule of relative intensity 1). \square

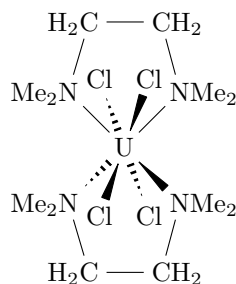
- II) The enthalpies of reaction of trimethylboron with NH_3 , CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, and $(\text{CH}_3)_3\text{N}$ are -58 , -74 , -81 , and -74 kJ/mol, respectively. Why is trimethylamine out of sequence?

Answer. Trimethylboron is not a very small lewis acid like BH_3 or H^+ . Thus, its own steric bulk clashes with the considerable bulk of $(\text{CH}_3)_3\text{N}$, hindering the reaction in a non-negligible fashion. This hindrance lowers the magnitude of the reaction enthalpy more than the additional electron-donating methyl group can raise it. \square

- III) The complex $\text{UCl}_4(\text{tmeda})_2$ (where tmeda is an abbreviation for $\text{Me}_2\text{N}-\text{CH}_2\text{CH}_2-\text{NMe}_2$, which binds by chelation to metals through both N-atoms) has been shown by X-ray crystallography to have almost perfect D_{2d} symmetry. Carefully draw a stereochemically accurate picture of this 8-coordinate uranium complex based on what you know about geometrical preferences in 8-coordinate complexes.

Answer. The possible molecular geometries for an 8-coordinate species are dodecahedral and square antiprismatic. Assuming all identical, monodentate ligands, the geometries' respective point groups are D_{2d} and D_{4d} . Based on this, dodecahedral might look more appealing, but since we have two bidentate chelating ligands, the D_{4d} square anti-prismatic form provides the wiggle room we need for the "descent in symmetry" these ligands will inevitably cause.

As such, if we take a square antiprismatic geometry and place our bidentate ligands opposite each other, we will have constructed the following D_{2d} molecule.



□