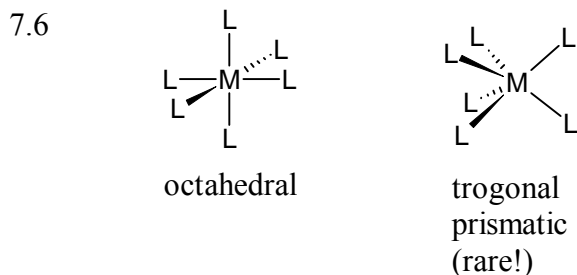
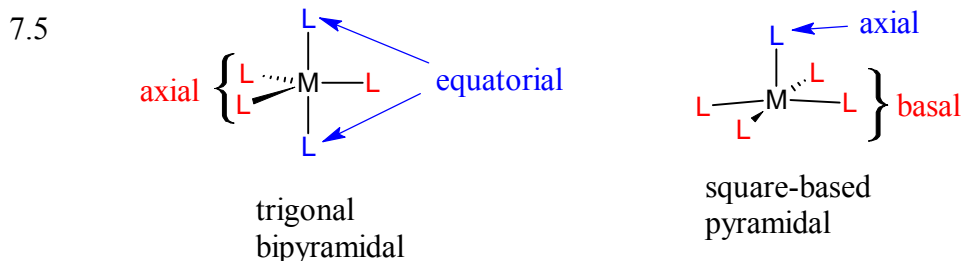
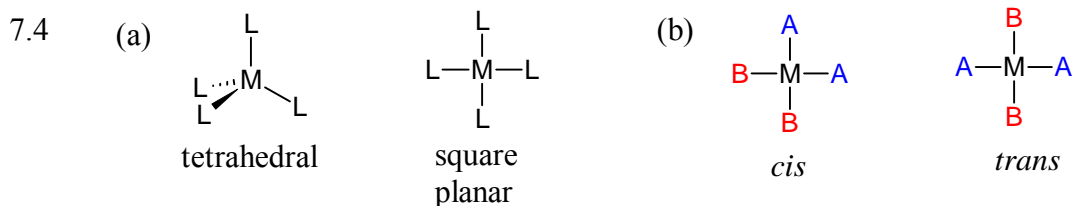


Section 6 – Questions from Shriver and Atkins

4.35 Remember, softness increases as you go down a group, and both Zn and Hg are in Group 12. Hg^{2+} is a very soft acid, so it is only realistically able to form compounds with the soft sulfide bases. Zn^{2+} , on the other hand, is relatively much harder (it's listed as "borderline" hard/soft in Table 4.5), so it can form bonds with sulfides (soft base) but also oxides (hard base).

- 4.p5 (a) <1 (softs and hard are together on the reactant side)
 (b) >1 (Cu^+ is softer than Cu^{2+} , so I^- should be with Cu^+ and Cl^- with Cu^{2+})
 (c) >1 ($\text{p}K_a$ of H_2O is much smaller than that of NH_3)



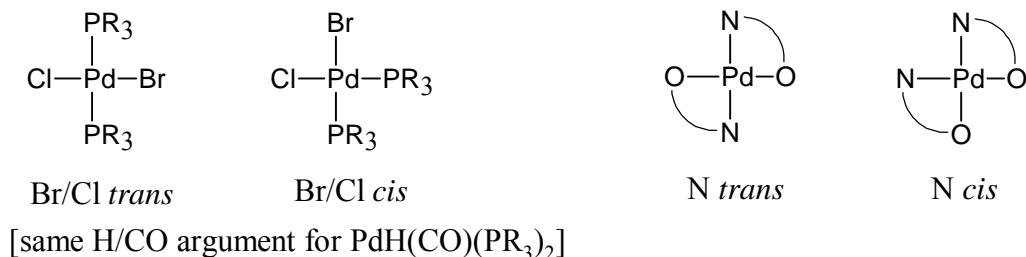
7.7 Dentate = "toothed", or the number of attachment points on the ligand. Thus, monodentate = 1-toothed (one attachment point), bidentate = 2-toothed; tetradentate = 4-toothed.

7.8 Ambidentate means there are two different attachment points (and, the ligand can only attach to one of them at a time – they are not bidentate chelates). The classic example (which we used in Experiment 4) is thiocyanate, $:\text{N}\equiv\text{C}-\text{S}::^-$, which can attach through the N or the S lone pair, but the N and S could not simultaneously attach to the same metal (because they point 180° from each other).

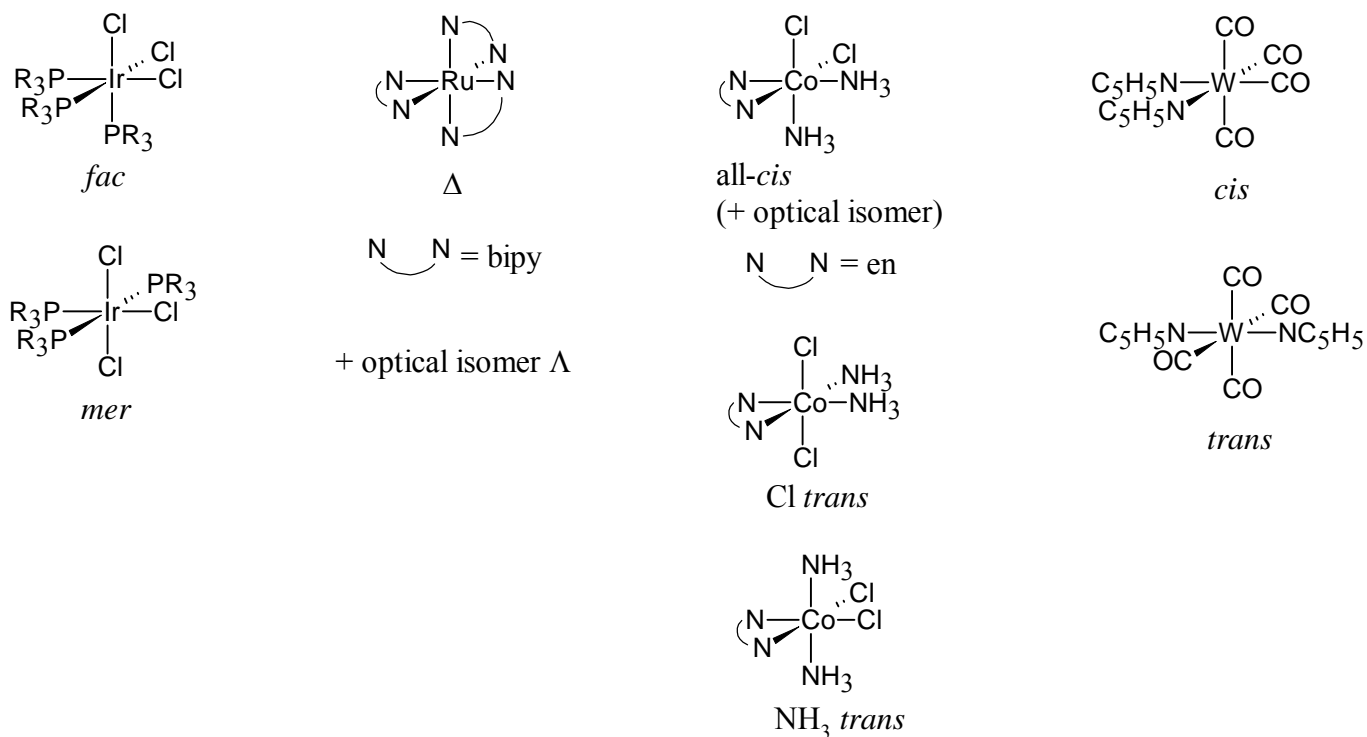
7.9 (b) (two phosphoruses), (c) (two nitrogens), and (d) (two nitrogens) are all bidentate. Note that the O lone pairs on (a) are not available for bonding, only the single P. (b) and (c) could geometrically attach to the same metal, so these two are chelates.

7.12 Only the last compound has two isomers, the R and S optical isomers.

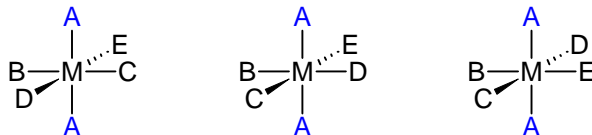
7.13 It is most useful to think in terms of *trans* pairs when making square-planar or octahedral isomers. Only 1 isomer is available for $\text{Pt}(\text{NH}_3)_2(\text{ox})$ because the oxalato ligand must be *cis*-oriented. The other three all have geometric isomers, as shown:



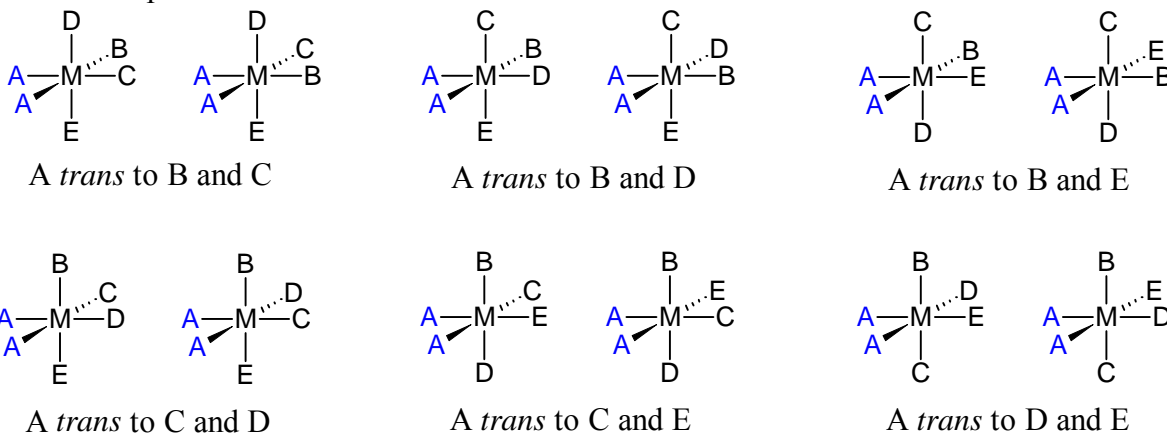
7.14 Only 1 isomer for $[\text{FeCl}(\text{OH}_2)_5]^{2+}$. Again, for all others, it's helpful to look at the *trans* pairs. Not that the chelating ligands en (1,2-ethylenediamine) and bipy (2,2'-bipyridine) must chelate on *cis* positions.



7.15 This is 6 monodentate ligands. Only cases where A are *trans* will there be an S_n axis (in this case a mirror plane $S_1 = \sigma$) and therefore be achiral. They are (B/C *trans*, B/D *trans*, and B/E *trans*):

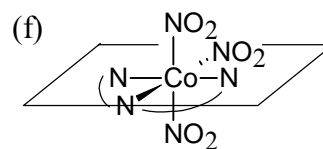
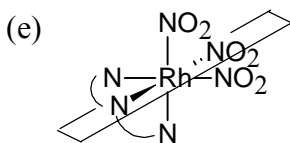
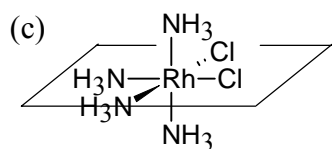


In cases where the two A ligands are *cis*, the result will be a chiral molecule. I have arranged them in enantiomeric pairs:

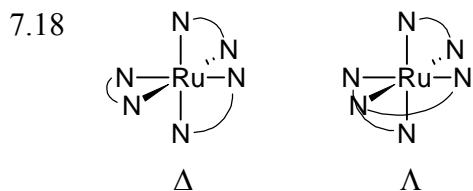


Grand total (all isomers, including optical) is 15.

7.16 Compounds (a) and (d) are chiral. Compound (b) is planar and therefore has a mirror plane! For the other achiral molecules, the mirror planes (S_1 axes) are:



7.17 This is the Δ isomer.



15.5 The short answer is that N_2 is not a good ligand (CO is toxic because it forms a non-reversible bond with the iron in heme proteins, N_2 does not bind to proteins). *Ipso facto* this means that the N-M bond is much weaker than the M-C bond.

- 20.1 (a) Co^{3+} is d^6 , NH_3 is a strong ligand, and Table 20.1 suggests (as expected) that $\text{Co}(\text{NH}_3)_6^{3+}$ is low spin with $\Delta_O = 22\,900\text{ cm}^{-1}$. Therefore, there are 0 unpaired electrons with configuration $t_{2g}^6 e_g^0$.
- (b) Fe^{2+} is d^6 , H_2O is a weaker ligand than NH_3 , so $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ is high spin with $\Delta_O = 10\,400\text{ cm}^{-1}$ (according to Table 20.1). Therefore, there are 4 unpaired electrons with configuration $t_{2g}^4 e_g^2$.
- (c) Fe^{3+} is d^5 , CN^- is a very strong ligand (and Fe^{3+} is stronger than Fe^{2+}), so we have low spin $t_{2g}^5 e_g^0$ (Table 20.1 says the $\Delta_O = 35\,000\text{ cm}^{-1}$) with 1 unpaired electron.
- (d) Cr^{3+} is d^3 , so the configuration is $t_{2g}^3 e_g^0$, with 3 unpaired electrons ($\Delta_O = 21\,500\text{ cm}^{-1}$).
- (e) Everything heavier than Zn is low spin, therefore W^0 is d^6 with 0 unpaired electrons in configuration $t_{2g}^6 e_g^0$. (Note that elemental W^0 would be $s^2 d^4$, but molecular W^0 is generally considered to be d^6).
- (f) Tetrahedral are always high spin, therefore Fe^{2+} is d^6 with configuration $e^3 t_2^3$ and 4 unpaired e^- .
- (g) Molecular Ni^0 is d^{10} with configuration $e^4 t_2^6$ and 0 unpaired e^- .
- 20.2 H^- has no π -symmetry orbitals, it is a strong-field ligand because it is a very strong σ -donor. Thus, π -accepting character is not a requirement for strong-field ligands.
- 20.3 This question uses the formula $\mu = [N(N+2)]^{1/2} \mu_B$, where N is the number of unpaired electrons.
 (a) $0\ \mu_B$ (b) $4.90\ \mu_B$ (c) $1.41\ \mu_B$ (d) $3.87\ \mu_B$ (e) 0 (f) $4.90\ \mu_B$ (g) 0
- 20.4 The strength of the ligands are $\text{NH}_3 > \text{H}_2\text{O} > \text{Cl}^-$, or the size of Δ_O/Δ_t should decrease along $\text{Co}(\text{NH}_3)_6^{2+} > \text{Co}(\text{H}_2\text{O})_6^{2+} \gg \text{CoCl}_4^{2-}$. Referring to Fig. 8-13 (colour wheel):
 looks purple = absorbing yellow
 looks yellow = absorbing purple
 looks pink = absorbing green/blue (?)
 In order of absorbing colours, then: purple > green/blue > yellow
 compound: $\text{Co}(\text{NH}_3)_6^{2+} > \text{Co}(\text{H}_2\text{O})_6^{2+} > \text{CoCl}_4^{2-}$
- 20.5 (a) Assuming both are high spin, $\text{Cr}(\text{OH}_2)_6^{2+}$ must have a larger LFSE (because Mn^{2+} is d^5 with 0 LFSE).
- (b) These are both d^5 so both have LFSE = 0.
- (c) H_2O is weak (high spin d^5 has 0 LFSE) and CN^- is strong (therefore low spin d^5 $\text{Fe}(\text{CN})_6^{3-}$ has a larger LFSE).
- (d) Both low-spin d^5 , but Δ_O for Ru^{3+} is stronger than for Fe^{3+} , therefore $\text{Ru}(\text{CN})_6^{3-}$ has larger LFSE.
- (e) Tetrahedral = high spin; Fe^{2+} is d^6 (one extra e electron) while Co^{2+} is d^7 (two extra e electrons), therefore CoCl_4^{2-} has a larger LFSE.

- 20.7 If the viewing colour is going from red to violet, the absorbed radiation is going from blue to yellow. We are also seeing the two orbitals get closer together (whatever 2 orbitals the transition involves), which makes sense because the wavelength is getting longer (lower energy transition), which means you go from low spin to high spin. Because we are going from square planar (non-coordinating anion) to something that is closer to octahedral (with the coordinating SCN^- anions), the orbitals in question must be the d_{z^2} and $d_{x^2-y^2}$.
- 20.8 Assuming the combination of Cr^{2+} and H_2O ligands are weak field, this leads to a high-spin d^4 configuration. Thus, with one electron in the degenerate e_g orbitals, this is a prime candidate for a Jahn-Teller distortion. The result would likely be a compound with two (*trans*) H_2O bonds being longer (distortion from point group O_h to D_{4h}).
- 20.9 Although not strictly a Jahn-Teller distortion, any degenerate orbital-filling could lead to a distortion. In the case of a d^1 system, the orbitals involved have π -symmetry, so this distortion would likely need a π -donor ligand to take place. Luckily, H_2O is such a ligand, so the molecule could distort by shortening in the plane of 4 ligands, which would lower the d_{xy} + ligand π -bonding orbital while raising the (empty) π^* orbital (which is in the t_{2g} set). At the same time, the (filled) d_{xz} and d_{yz} π -bonding orbitals would raise a little, but the corresponding π^* orbitals in the t_{2g} set would lower, meaning that the lone e^- in those orbitals would go down in energy. Thus, the net effect is empty π^* goes up, partly-filled π^* goes down for a net saving in energy following the distortion.