

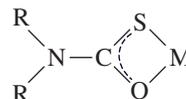
Problems

- 10.1** Predict the number of unpaired electrons for each of the following:
- a tetrahedral d^6 ion
 - $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
 - a square-planar d^7 ion
 - a coordination compound with a magnetic moment of 5.1 Bohr magnetons
- 10.2** Identify the *first-row* transition metal **M** that satisfies the requirements given (more than one answer may be possible):
- $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ having one unpaired electron
 - $[\text{MBr}_4]^-$ having the most unpaired electrons
 - diamagnetic $[\text{M}(\text{CN})_6]^{3-}$
 - $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ having $\text{LFSE} = -\frac{3}{5} \Delta_o$
- 10.3** Identify the most likely transition metal **M**:
- $\text{K}_3[\text{M}(\text{CN})_6]$, in which **M** is a first-row transition metal and the complex has three unpaired electrons
 - $[\text{M}(\text{H}_2\text{O})_6]^{3+}$, in which **M** is a second-row transition metal and $\text{LFSE} = -2.4 \Delta_o$
 - tetrahedral $[\text{MCl}_4]^-$, which has five unpaired electrons and first-row transition metal **M**
 - the third row d^8 transition metal in the square-planar complex $\text{MCl}_2(\text{NH}_3)_2$, which has two **M**–Cl stretching bands in the IR
- 10.4** The stepwise stability constants in aqueous solution at 25°C for the formation of the ions $[\text{M}(\text{en})(\text{H}_2\text{O})_4]^{2+}$, $[\text{M}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$, and $[\text{M}(\text{en})_3]^{2+}$ for copper and nickel are given in the table. Why is there such a difference in the third values? (Hint: Consider the special nature of d^9 complexes.)

	$[\text{M}(\text{en})(\text{H}_2\text{O})_4]^{2+}$	$[\text{M}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$	$[\text{M}(\text{en})_3]^{2+}$
Cu	3×10^{10}	1×10^9	0.1 (estimated)
Ni	2×10^7	1×10^6	1×10^4

- 10.5** A first-row transition-metal complex of formula $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ has a magnetic moment of 3.9 Bohr magnetons. Determine the most likely number of unpaired electrons and the identity of the metal.
- 10.6** Predict the magnetic moments (spin-only) of the following species:
- $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Cr}(\text{CN})_6]^{4-}$
 - $[\text{FeCl}_4]^-$
 - $[\text{Fe}(\text{CN})_6]^{3-}$
 - $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$
- 10.7** A compound with the empirical formula $\text{Fe}(\text{H}_2\text{O})_4(\text{CN})_2$ has a magnetic moment corresponding to $2\frac{2}{3}$ unpaired electrons per iron. How is this possible? (Hint: Two octahedral Fe(II) species are involved, each containing a single type of ligand.)
- 10.8** What are the possible magnetic moments of Co(II) in tetrahedral, octahedral, and square-planar complexes?

- 10.9** Monothiocarbamate complexes of Fe(III) have been prepared. (See K. R. Kunze, D. L. Perry, L. J. Wilson, *Inorg. Chem.*, **1977**, *16*, 594.) For the methyl and ethyl complexes, the magnetic moment, μ , is 5.7 to 5.8 μ_B at 300 K; it changes to 4.70 to 5 μ_B at 150 K, and drops still further to 3.6 to 4 μ_B at 78 K. The color changes from red to orange as the temperature is lowered. With larger R groups (propyl, piperidyl, pyrrolidyl), $\mu > 5.3 \mu_B$ at all temperatures and greater than 6 μ_B in some. Explain these changes. Monothiocarbamate complexes have the following structure.



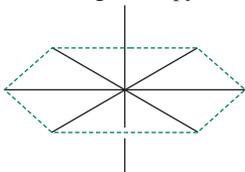
- 10.10** Show graphically how you would expect ΔH for the reaction $[\text{M}(\text{H}_2\text{O})_6]^{2+} + 6 \text{NH}_3 \longrightarrow [\text{M}(\text{NH}_3)_6]^{2+} + 6 \text{H}_2\text{O}$ to vary for the first transition series ($\text{M} = \text{Sc}$ through Zn).
- 10.11** Using the coordinate system in Figure 10.17, verify the characters of Γ_σ and Γ_π in Table 10.9 and show that these representations reduce to $A_1 + T_2$ and $E + T_1 + T_2$, respectively.
- 10.12** Using the angular overlap model, determine the energies of the d orbitals of the metal for each of the following geometries, first for ligands that act as σ donors only and second for ligands that act as both σ donors and π acceptors. Angular overlap energy-level diagrams are required for each possibility.
- linear ML_2
 - trigonal-planar ML_3
 - square-pyramidal ML_5
 - trigonal-bipyramidal ML_5
 - cubic ML_8 (Hint: A cube is two superimposed tetrahedra.)
- 10.13** Use the angular overlap method to calculate the energies of both ligand and metal orbitals for *trans*- $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$, taking into account that ammonia is a stronger σ -donor ligand than chloride, but chloride is a stronger π donor. Use the 1 and 6 positions for the chloride ions.
- 10.14** Consider a transition-metal complex of formula $\text{ML}_4\text{L}'$. Using the angular overlap model and assuming trigonal-bipyramidal geometry, determine the energies of the d orbitals
- considering sigma interactions only (assume L and L' are similar in donor ability).
 - considering L' as a π acceptor as well. Consider L' in both (1) axial and (2) equatorial positions.
 - based on the preceding answers, would you expect π -acceptor ligands to preferentially occupy axial or equatorial positions in five-coordinate complexes? What other factors should be considered in addition to angular overlap?

- 10.15** On the basis of your answers to Problems 10.13 and 10.14, which geometry, square-pyramidal or trigonal-bipyramidal, is predicted to be more likely for five-coordinate complexes by the angular overlap model? Consider both σ -donor and combined σ -donor and π -acceptor ligands.
- 10.16** The common structures having $CN = 4$ for transition-metal complexes are tetrahedral and square planar. However, these are not the only conceivable structures. Examples of main group compounds having *seesaw* structures are known, and *trigonal-pyramidal* structures may also be possible in some cases.



Seesaw Trigonal Pyramidal

- a.** For these structures, determine the relative energies of the d orbitals of a transition-metal complex of formula ML_4 in which L is a σ donor only.
- b.** Considering both high-spin and low-spin possibilities, calculate the energy of each configuration, d^1 to d^{10} , in terms of e_σ .
- c.** For which configurations is the seesaw structure favored? The trigonal-pyramidal structure? Neither?
- 10.17** A possible geometry for an eight-coordinate complex ML_8 might be a hexagonal bipyramid:



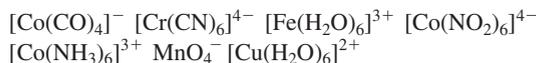
- a.** Predict the effect of the eight ligands on the energies of the d orbitals of a metal M, using the angular overlap model and assuming that the ligands are sigma donors only. [Note: To determine the values of e_σ , you will need to add two more positions to Table 10.11.]
- b.** Assign the symmetry labels of the d orbitals (labels of the irreducible representations).
- c.** Repeat the calculations in part **a** for a ligand that can act both as a σ donor and a π acceptor.
- d.** For this geometry, and assuming low spin, which d^n configurations would be expected to give rise to Jahn–Teller distortions?
- 10.18** $[Co(H_2O)_6]^{3+}$ is a strong oxidizing agent that will oxidize water, but $[Co(NH_3)_6]^{3+}$ is stable in aqueous solution. Rationalize this observation by comparing the difference in LFSE for each pair of oxidized and reduced complexes (that is, the differences in LFSE between $[Co(H_2O)_6]^{3+}$ and $[Co(H_2O)_6]^{2+}$, and between $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{2+}$). Table 10.6 gives data on the aqueous complexes; Δ_o for $[Co(NH_3)_6]^{2+}$ is $10,200\text{ cm}^{-1}$, and Δ_o for $[Co(NH_3)_6]^{3+}$ is about $24,000\text{ cm}^{-1}$. The Co(III)

complexes are low-spin complexes and the Co(II) complexes are high spin.

- 10.19** Explain the order of the magnitudes of the following Δ_o values for Cr(III) complexes in terms of the σ and π donor and acceptor properties of the ligands.

Ligand	F^-	Cl^-	H_2O	NH_3	en	CN^-
Δ_o (cm^{-1})	15,200	13,200	17,400	21,600	21,900	33,500

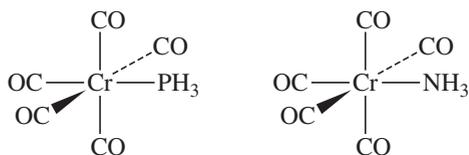
- 10.20** Oxygen is more electronegative than nitrogen; fluorine is more electronegative than the other halogens. Fluoride is a stronger field ligand than the other halides, but ammonia is a stronger field ligand than water. Provide a model consistent with these observations.
- 10.21** **a.** Explain the effect on the d -orbital energies when an octahedral complex is compressed along the z axis.
b. Explain the effect on the d -orbital energies when an octahedral complex is stretched along the z axis. In the limit, this results in a square-planar complex.
- 10.22** Solid CrF_3 contains a Cr(III) ion surrounded by six F^- ions in an octahedral geometry, all at distances of 190 pm. However, MnF_3 is in a distorted geometry, with Mn–F distances of 179, 191, and 209 pm (two of each). Explain.
- 10.23** **a.** Determine the number of unpaired electrons, magnetic moment, and ligand field stabilization energy for each of the following complexes:



- b.** Why are two of these complexes tetrahedral and the rest octahedral?
- c.** Why is tetrahedral geometry more stable for Co(II) than for Ni(II)?
- 10.24** The $2+$ ions in the first transition series generally show a preference for octahedral geometry over tetrahedral geometry. Nevertheless, the number of tetrahedral complexes formed is in the order $Co > Fe > Ni$.
- a.** Calculate the ligand field stabilization energies for tetrahedral and octahedral symmetries for these ions. Use the differences in LFSE for octahedral versus tetrahedral geometries to assess the relative stabilities of the possible configurations. Use the estimate that $\Delta_t = \frac{4}{9}\Delta_o$ to express LFSE values in terms of Δ_o . Consider both high- and low-spin cases as appropriate for the octahedral complexes. Do these numbers explain this order?
- b.** Does the angular overlap model offer any advantage in explaining this order? To make this assessment, determine the differences between the electronic configuration energies for octahedral and tetrahedral geometries using the angular overlap model. Consider both high- and low-spin situations as appropriate.
- 10.25** Except in cases in which ligand geometry requires it, square-planar geometry occurs most commonly with

d^7 , d^8 , and d^9 ions and with strong-field, π -acceptor ligands. Suggest why these conditions support square-planar geometry.

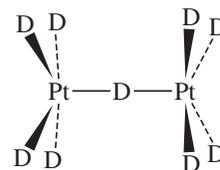
- 10.26** Use the group theory approach of Section 10.7 to prepare an energy-level diagram for
- a square-pyramidal complex.
 - a pentagonal-bipyramidal complex.
- 10.27** Cobalt(I) complexes are relatively rare compared to Co(II) and Co(0), but the complexes $\text{CoX}(\text{PPh}_3)_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are known with approximate tetrahedral coordination geometry about the high spin d^8 metal center. The angular overlap model was used to analyze the electronic structure of $\text{CoCl}(\text{PPh}_3)_3$, where three independent molecules (with very similar yet statistically different bond lengths and angles) were observed in the unit cell (J. Krzystek, A. Ozarowski, S. A. Zvyagin, J. Tesler, *Inorg. Chem.*, **2012**, *51*, 4954). Using the angular overlap parameters for molecule 1 in Table 3 of this reference, generate an energy-level diagram for $\text{CoCl}(\text{PPh}_3)_3$. Does the electronic structure predicted by this method surprise you? Explain. On the basis of Table 3, the chloride ligands are better π donors, and the triphenylphosphine ligands better σ donors in $\text{NiCl}_2(\text{PPh}_3)_2$ relative to $\text{CoCl}(\text{PPh}_3)_3$. What is probably the most important factor that causes these differences?
- 10.28** Nitrogen monofluoride, NF, can serve as a ligand in transition-metal complexes.
- Prepare a molecular orbital energy-level diagram of the NF molecule, showing clearly how the atomic orbitals interact.
 - If NF can interact with a transition-metal ion to form a chemical bond, what type(s) of ligand–metal interactions would be most important? Would you expect NF to be high or low in the spectrochemical series? Explain.
- 10.29** Calculations have been reported on the changes that occur when the following compounds are oxidized by one electron. (See T. Leyssens, D. Peeters, A. G. Orpen, J. N. Harvey, *New J. Chem.*, **2005**, *29*, 1424–1430.)



- When these compounds are oxidized, what is the effect on the C–O distances? Explain.
 - When these compounds are oxidized, what is the effect on the Cr–P distance? On the Cr–N distance? Explain.
- 10.30** One of the more striking hydride complexes is ennea-hydridorhenate, $[\text{ReH}_9]^{2-}$, which has tricapped trigonal-pyramidal geometry. What is the point group of this ion? Construct a representation using the hydrogen orbitals as a basis. Reduce this to its component irreducible

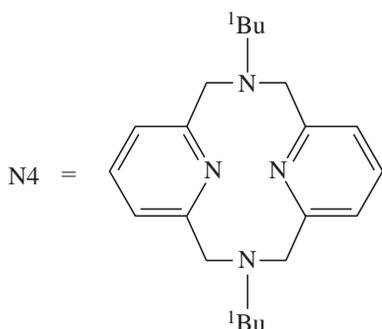
representations, and determine which orbitals of Re are of suitable symmetry to interact with the hydrogen group orbitals.

- 10.31** The linear molecule FeH_2 has been observed in the gas phase. (See H. Korsgen, W. Urban, J. M. Brown, *J. Chem. Phys.* **1999**, *110*, 3861.) Assume that the iron atom can potentially use s , p , and d orbitals to interact with the hydrogens. If the z axis is collinear with the molecular axis:
- Sketch the group orbitals of the hydrogen atoms that potentially could interact with the iron.
 - Show how the group orbitals and the central atom would interact.
 - Which interaction would you expect to be the strongest? The weakest? Explain briefly. (Note: Orbital potential energies can be found in Appendix B.9.)
- 10.32** Although CrH_6 has not been synthesized, this should not prevent us from considering what its properties might be! The bonding in CrH_6 and other related small molecules of theoretical interest has been investigated. (R. J. Gillespie, S. Noury, J. Pilme, B. Silvi, *Inorg. Chem.*, **2004**, *43*, 3248). Sketch a molecular orbital diagram (energy-level diagram), showing interactions between metal d orbitals and relevant ligand orbitals in CrH_6 , assuming octahedral geometry. Be sure to take into account orbital potential energies (Appendix B.9).
- 10.33** The ion $[\text{Pt}_2\text{D}_9]^{5-}$, shown below, has eclipsed geometry.
- What is the point group of this ion?
 - Assume that the platinum atoms can potentially use s , p , and d orbitals to interact with the central deuterium. If the z axis is chosen to be collinear with the principal axis of rotation:
 - Sketch the group orbitals of the platinum atoms that potentially could interact with the central D. Be sure to label all orbitals.
 - Show how the group orbitals and the central atom would interact.
 - Which interaction would you expect to be the strongest, and why?



- 10.34** On the basis of molecular orbitals, explain why the Mn–O distance in $[\text{MnO}_4]^{2-}$ is longer (by 3.9 pm) than in $[\text{MnO}_4]^-$. (See G. J. Palenik, *Inorg. Chem.*, **1967**, *6*, 503, 507.)
- 10.35** The square-planar preference of Pd(II) is clearly evident in $(\text{N}4)\text{Pd}(\text{CH}_3)\text{Cl}$ ($\text{N}4 = N,N'$ -di-*tert*-butyl-2,11-diaza[3.3](2,6)pyridinophane) (J.R. Khusnutdinova, N. P. Rath, L. M. Mirica, *J. Am. Chem. Soc.*, **2010**, *132*, 7303). Although N4 is a potentially tetradentate ligand, two of the nitrogen atoms point away from the Pd center,

yielding a square-planar coordination geometry. This situation changes upon oxidation to afford a Pd(III) complex with a tetragonal geometry. Sketch the structure of the (N4)Pd(CH₃)Cl oxidation product, and label the bond lengths with their distances to provide the argument for the Jahn–Teller distortion. Which metal *d* orbital is believed to contribute the most to the HOMO of the oxidized complex? Without changing any of the donor atoms, how might the ligand be subtly modified to cause this HOMO to *increase* in energy? Sketch the modified ligand you would introduce and explain the reasoning for your selection in terms of why it might raise the HOMO energy.



- 10.36** Clusters containing multiple metal ions with large spin values and Jahn–Teller distortions can exhibit ferromagnetism independently, and are called *single-molecule magnets*. Reaction of {2-[(3-methylaminoethylimino)methyl]-phenol} (HL¹) with manganese(II) acetate and sodium azide in methanol resulted in the Mn(III) dimer [MnL¹(N₃)(OCH₃)₂]₂. Sketch this complex and use bond length arguments to discuss the most obvious result of Jahn–Teller distortion (S. Naiya, S. Biswas, M. G. B. Drew, C. J. Gómez-García, A. Ghosh, *Inorg. Chem.*, **2012**, *51*, 5332).
- 10.37** The potentially tridentate 1,4,7-triazacyclononane (tacn) is used extensively. Tri-protonated tacn reacts with K₂PdCl₄ affording salts of [Pd(tacn)(Htacn)]³⁺ with one of the unbound nitrogen atoms cationic (A. J. Blake, L. M. Gordon, A. J. Holder, T. I. Hyde, G. Reid, M. Schröder, *J. Chem. Soc., Chem. Commun.*, **1988**, 1452). What structural feature of [Pd(tacn)(Htacn)]³⁺ is surprising? How do the authors rationalize this feature? Propose an alternative explanation keeping in mind that the hydrogen that results in the positively charged and non-Pd bound nitrogen could not be located in the Figure 1 drawing. Oxidation of [Pd(tacn)₂]²⁺ affords [Pd(tacn)₂]³⁺. Sketch the [Pd(tacn)₂]³⁺ structure (incorrectly identified in Figure 3 of the reference), and label the bond lengths (with their distances) that define its Jahn–Teller distortion.

The following problems require the use of molecular modeling software.

- 10.38** The ion [TiH₆]²⁻ has been found to have O_h symmetry. (See I. B. Bersuker, N. B. Balabanov, D. Pekker, J. E. Boggs, *J. Chem. Phys.* **2002**, *117*, 10478.)
- Using the H orbitals of the ligands as a basis, construct a reducible representation (the symmetry equivalent of a collection of group orbitals) for this ion.
 - Reduce this representation to its irreducible components.
 - Which orbitals of Ti are suitable for interaction with each of the results from part **b**?
 - Show the interactions of *d* orbitals of Ti with the appropriate group orbital(s), labeled to show the matching irreducible representations, in an energy-level diagram. Identify Δ_o on this diagram. (Note: Useful orbital potential energies can be found in Appendix B.9.)
 - Now use molecular modeling software to calculate and display the molecular orbitals of [TiH₆]²⁻. Compare the results with your work in part **d** and with Figure 10.5, and comment on the similarities and differences.
- 10.39** Calculate and view the molecular orbitals of the octahedral ion [TiF₆]³⁻.
- Identify the *t_{2g}* and *e_g* bonding and antibonding orbitals, and indicate which *d* orbitals of Ti are involved in each.
 - Compare your results with Figures 10.5 and 10.7. Do they indicate that fluoride is acting as a π donor as well as σ donor?
- 10.40** Reaction of many iron(III) compounds with hydrochloric acid yield the tetrahedral [FeCl₄]⁻ ion. Calculate and view the molecular orbitals of this ion.
- Identify the *e* and *t₂* orbitals involved in Fe–Cl bonding (see Figures 10.18 and 10.19), and indicate which *d* orbitals of Fe are involved in each.
 - Compare your results with Figure 10.19. Comment on the similarities and differences.
- 10.41** Table 10.12 provides values of Δ_o for eight octahedral complexes of chromium(III). Select three of the ligands listed, draw the structures of their octahedral complexes of Cr(III), and calculate and view the molecular orbitals. Identify the *t_{2g}* and *e_g* orbitals, record the energy of each, and determine the Δ_o values. Is your trend consistent with the values in the table? (Note: The results are likely to vary significantly with the level of sophistication of the software used. If you have several molecular modeling programs available, you may want to try different ones to compare their results.)