- S19.9 Assign the bands in the spectrum of $[Cr(NCS)_6]^3$? This six-coordinate d^3 complex undoubtedly has O_h symmetry, so the general features of its spectrum will resemble the spectrum of $[Cr(NH_3)_6]^{3+}$, shown in Figure 19.19. The very low intensity of the band at 16,000 cm⁻¹ is a clue that it is a spin-forbidden transition, probably ${}^2E_g \leftarrow {}^4A_{2g}$. Spin-allowed but Laporte-forbidden bands typically have $\varepsilon \sim 100 \text{ M}^{-1} \text{ cm}^{-1}$, so it is likely that the bands at 17,700 cm⁻¹ and 23,800 cm⁻¹ are of this type (they correspond to the ${}^4T_{2g} \leftarrow {}^4A_{2g}$ and ${}^4T_{1g} \leftarrow {}^4A_{2g}$ transitions, respectively). The band at 32,400 cm⁻¹ is probably a charge transfer band, since its intensity is too high to be a ligand field (d-d) band. Since you are provided with the hint that the NCS⁻ ligands have low-lying π^* orbitals, it is reasonable to conclude that this band corresponds to a MLCT transition. Notice that the two spin-allowed ligand field transitions of $[Cr(NCS)_6]^{3-}$ are at lower energy than those of $[Cr(NH_3)_6]^{3+}$, showing that NCS⁻ induces a smaller δ_0 on Cr³⁺ than does NH₃. Also notice that $[Cr(NH_3)_6]^{3+}$ lacks an intense MLCT band at ~30,000-40,000 cm⁻¹, showing that NH₃ does not have low-lying empty orbitals.
- **19.1** Configuration, number of unpaired electrons, and LFSE? (a) $[Co(NH_3)_6]^{3+}$? Since the NH₃ ligands are neutral, the cobalt ion in this octahedral complex is Co^{3+} , which is a d^6 metal ion. Ammonia is in the middle of the spectrochemical series but, since the cobalt ion has a 3+ charge, this is a strong field complex and hence is low spin, with S = 0 and no unpaired electrons (the configuration is t^2g^6). The LFSE is $6(0.4\Delta_0) = 2.4\Delta_0$. Note that this is the largest possible value of LFSE for an octahedral complex.

(b) $[Fe(OH_2)_6]^{2+2}$ The iron ion in this octahedral complex, which contains only neutral water molecules as ligands, is Fe²⁺, which is a d^6 -metal ion. Since water is lower in the spectrochemical series than NH₃ (i.e., it is a weaker field ligand than NH₃) and since the charge on the metal ion is only 2+, this is a weak field complex and hence is high spin, with S = 2 and four unpaired electrons (the configuration is $t_{2g}^4 e_g^2$). The LFSE is $4(0.4\Delta_0) - 2(0.6\Delta_0) = 0.4\Delta_0$. Compare this small value to the large value for the low spin d^6 complex in part (a) above.

(c) $[Fe(CN)_6]^{3-2}$ The iron ion in this octahedral complex, which contains six negatively charged CN⁻ ion ligands, is Fe³⁺, which is a d^5 -metal ion. Cyanide ion is a very strong-field ligand, so this is a strong-field complex and hence is low spin, with S = 1/2 and one unpaired electron. The configuration is t_{2g}^{5} and the LFSE is $2.0\Delta_0$.

(d) $[Cr(NH_3)_6]^{3+}$? The complex contains six neutral NH₃ ligands, so chromium is Cr^{3+} , a d^3 metal ion. The configuration is t_{2g}^3 , and so there are three unpaired electrons and S = 3/2. Note that, for octahedral complexes, only d^4-d^7 metal ions have the possibility of being either high spin or low spin. For $[Cr(NH_3)_6]^{3+}$, the LFSE = $3(0.4\Delta_0) = 1.2\Delta_0$. (For d^4-d^3 , d^8 , and d^9 metal ions in octahedral complexes, only one spin state is possible.)

(e) [W(CO)₆]? Carbon monoxide (i.e., the carbonyl ligand) is neutral, so this is a complex of W(0). The W atom in this octahdral complex is d^6 . Since CO is such a strong field ligand (it is even higher in the spectrochemical series than CN⁻), W(CO)₆ is a strong-field complex and hence is low spin, with no unpaired electrons (the configuration is t_{2g}^3). The LFSE = $6(0.4\Delta_0) = 2.4\Delta_0$.

(f) Tetrahedral [FeCl₄]²⁻? The iron ion in this complex, which contains four negatively charged Cl⁻ ion ligands, is Fe²⁺, which is a d^6 metal ion. All tetrahedral complexes are high spin, since Δ_T is much smaller than Δ_0 ($\Delta_T = (4/9)\Delta_0$, if the metal ion, the ligands, and the metal-ligand distances are kept constant), so for this complex S = 2 and there are four unpaired electrons. The configuration is $e^3 t^3$. The LFSE is $3(0.6\Delta_T) - 3(0.4\Delta_T) = 0.6 \Delta_T$.

(g) Tetrahedral [Ni(CO)₄]? The neutral CO ligands require that the metal center in this complex is Ni⁰, which is a d^{10} -metal atom. Regardless of geometry, complexes of d^{10} -metal atoms or ions will never have any unpaired electrons and will always have LFSE = 0, and this complex is no exception. $e^{4}t^{4}$

- **19.2** What factors account for the ligand field strength of different ligands? It is clear that π -acidity cannot be a requirement for a position high in the spectrochemical series, since H⁻ is a very strong field ligand but is not a π -acid (it has no *low energy* acceptor orbitals of local π -symmetry). However, ligands that are very strong σ -bases will increase the energy of the e_g orbitals in an octahedral complex relative to the t_{2g} orbitals. Thus there are two ways for a complex to develop a large value of Δ_0 , by possessing ligands that are π -acids or by possessing ligands that are strong σ -bases (of course some ligands, like CN⁻, exhibit both π -acidity and moderately strong σ -basicity). A class of ligands that are also very high in the spectrochemical series are alkyl anions, R⁻ (e.g., CH₃⁻). These are not π -acids but, like H⁻, are very strong bases.
- **19.3** Estimate the spin-only contribution to the magnetic moment? The formula for the spin-only moment is $\mu_{SO} = [(N)(N+2)]^{1/2}$. Therefore, the spin-only contributions are:

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complex	N	$\mu_{\rm SO} = \left[(N)(N+2) \right]^{1/2}$
$[Co(NH_3)_6]^{3+}$	0	of a second statement of the proceed of the second of the
$[Fe(OH_2)_6]^{2+}$	4	4.9
$[Fe(CN)_{6}]^{3-}$	1	1.7
$[Cr(NH_3)_6]^{3+}$	3	3.9
[W(CO) ₆]	0	0
$[FeCl_4]^{2-}$	4	4.9
[Ni(CO) ₄]	0	0

- Assign the colors pink, yellow, and blue to cobalt(II) complexes? The colors of metal complexes are 19.4 frequently caused by ligand-field transitions involving electron promotion from one subset of d orbitals to another (e.g., from t_{2g} to e_g for octahedral complexes or from e to t_2 for tetrahedral complexes). Of the three complexes given, the lowest energy transition probably occurs for $[CoCl_4]^{2-}$, because it is tetrahedral (Δ_T = $(4/9)(\Delta_0)$ and because Cl⁻ is a weak-field ligand. This complex is blue, since a solution of it will absorb low energy red light and reflect the complement of red, which is blue. Of the two complexes that are left $[Co(NH_3)_6]^{2+}$ probably has a higher energy transition than $[Co(OH_2)_6]^{2+}$, since NH₃ is a stronger-field ligand than H₂O (see Table 19.1). The complex $[Co(NH_3)_6]^{2+}$ is yellow because only a small amount of visible light. at the blue end of the spectrum, is absorbed by a solution of this complex. By default, you should conclude that $[Co(OH_2)_6]^{2+}$ is pink.
- Larger LFSE? (a) The chromium is expected to have a larger crystal field stabilization because of the table 19.5 $e_{v}1$ configuration $[(0.4 \times 3) - (0.6 \times 1) = 0.6 \Delta_{0}]$ compared to the Manganese with an electronic configuration $t_{2v}3e_v2[(0.4 \times 3) - (0.6 \times 2) = 0].$

(b) Although Fe^{3+} and Mn^{2+} are iso-electronic, the higher charge on the Fe ion leads to higher stabilization energy.

(c) Since water is a weak-field ligand compared to CN-, the electronic configurations of these two complexes differ. For the $[Fe(CN)_6]^{3-}$ the configuration will be $t_{2g}5 e_g0 [(0.4 \times 5) = 2 \Delta_0]$ while the corresponding configuration for the aquo complex will be $t_{2g}3 e_g 2 [(0.4 \times 3) - (0.6 \times 2) = 0]$. Hence $[Fe(CN)_6]^{3-}$ will have higher stabilization.

(d) The LFSE increases down the group and hence the ruthenium complex will have higher stabilization.

(e) In general, tetrahedral complexes form high-spin complexes. Fe²⁺ with an electronic configuration of t_{2g} 3 will have smaller stabilization [(2 × 0.6) – (2 × 0.4) = 0.2 Δ_0] compared to Co²⁺ with a configuration of e $t_{2g} 3 [(4 \times 0.6) - (3 \times 0.4) = 1.2 \Delta_0].$

19.6

Comment on the lattice enthalpies for CaO, TiO, VO, MnO, FeO, CoO, and NiO? As in the answer to Exercise S19.3, there are two factors that lead to the values given in this question and plotted below decreasing ionic radius from left to right across the d block, leading to a general increase in ΔH_1 from CaO NiO, and LFSE, which varies in a more complicated way for high-spin metal ions in an octahedral environment, increasing from d^0 to d^3 , then decreasing from d^3 to d^5 , then increasing from d^5 to d^8 , then decreasing again from d^8 to d^{10} . The straight line through the black squares is the trend expected for the first factor, the decrease in ionic radius (the last black square is not a data point, but simply the extrapolation of the line between $\Delta H_{\rm L}$ values for CaO and MnO, both of which have LFSE = 0). The deviations of $\Delta H_{\rm L}$ values for TiO, VO, FeO, CoO, and NiO from the straight line are a manifestation of the second factor, the nonzero values of LFSE for Ti^{2+} , V^{2+} , Fe^{2+} , Co^{2+} , and Ni^{2+} . You will find in Chapter 23 that TiO and VO have considerable metal-metal bonding, and this factor also contributes to their stability.

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19.7 Diamagnetic and paramagnetic Ni(II) complexes? Perchlorate, ClO_4^- , is a very weakly basic anion (consider that $HClO_4$ is a very strong Brønsted acid). Therefore, in the compound containing Ni(II), the neutral macrocyclic ligand, and two ClO_4^- anions, there is probably a four-coordinate square-planar Ni(II) (d^8) complex and two noncoordinated perchlorate anions. Square-planar d^8 complexes are diamagnetic (see Figure 19.10), since they have a configuration (xz, $yz^4(xy)^2(z^2)^2$). When SCN ligands are added, they coordinate to the nickel ion, producing a tetragonal (D_{4b}) complex that has two unpaired electrons (configuration $t_{2e}^{-6}e_e^{-2}$).



19.8 Predict the structure of $[Cr(OH_2)_6]^{2^+}$? The main consequence of the Jahn-Teller theorem is that a nonlinear molecule or ion with an orbitally degenerate ground state is not as stable as a distorted version of the molecule or ion if the distortion removes the degeneracy. The high-spin d^4 complex $[Cr(OH_2)_6]^{2^+}$ has the configuration $t_{2g}^3 e_g^1$, which is orbitally degenerate since the single e_g electron can be in either the d_{22} or the d_{x2-y2} orbital. Therefore, by the Jahn-Teller theorem, the complex should not have O_h symmetry. A tetragonal distortion, whereby two *trans* metal-ligand bonds are elongated and the other four are shortened, removes the degeneracy. This is the most common distortion observed for octahedral complexes of high-spin d^4 , low-spin d^7 , and d^9 metal ions, all of which possess e_g degeneracies and exhibit measurable Jahn-Teller distortions. The predicted structure of the $[Cr(OH_2)_6]^{2^+}$ ion, with the elongation of the two *trans* Cr-O bonds shown greatly exaggerated, is shown at the right.





- **19.21** The origins of transitions for a complex of Co(III) with ammine and chloro ligands? Let's start with the intense band at relatively high energy with $\varepsilon_{max} = 2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. This is undoubtedly a spin-allowed charge-transfer transition, since it is too intense to be a ligand field (d-d) transition. Furthermore, it is probably an LMCT transition, not an MLCT transition, since the ligands do not have the empty orbitals necessary for an MLCT transition. The two bands with $\varepsilon_{max} = 60$ and $80 \text{ M}^{-1} \text{ cm}^{-1}$ are probably spin-allowed ligand field transitions. Even though the complex is not strictly octahedral, the ligand field bands are still not very intense. The very weak peak with $\varepsilon_{max} = 2 \text{ M}^{-1} \text{ cm}^{-1}$ is most likely a spin-forbidden ligand field transition.
- 19.22 Describe the transitions of Fe³⁺ impurities in bottle glass? The Fe³⁺ ions in question are d⁵ metal ions. If they were low spin, several spin-allowed ligand field transitions would give the glass a color even when viewed through the wall of the bottle (see the Tanabe-Sugano diagram for d⁵ metal ions in Resource Section 6). Therefore, the Fe³⁺ ions are high spin, and as such have no spin-allowed transitions (the ground state of an octahedral high-spin d⁵ metal ion is ⁶A_{1g}, and there are no sextet excited states). The faint green color, which is only observed when looking through a *long* pathlength of bottle glass, is caused by spin-forbidden ligand field transitions.
- **19.23** The origins of transitions for $[Cr(H_2O)_6]^{3+}$ and $CrO_4^{2-?}$ The blue-green color of the Cr^{3+} ions in $[Cr(H_2O)_6]^{3+}$ is caused by spin-allowed but Laporte-forbidden ligand field transitions. The relatively low molar absorption coefficient, ε , which is a manifestation of the Laporte-forbidden nature of the transitions, is the reason that the intensity of the color is weak. The oxidation state of chromium in dichromate dianion is Cr(VI), which is d^0 . Therefore, no ligand field transitions are possible. The intense yellow color is due to LMCT transitions (i.e., electron transfer from the oxide ion ligands to the Cr(VI) metal center). Charge transfer transitions are intense because they are both spin-allowed and Laporte-allowed.



19.24 The orbitals of $[CoCl(NH_3)_5]^{2+2}$. The d_z^2 orbital in this complex is left unchanged by each of the symmetry operations of the C_{4v} point group. It therefore has A₁ symmetry. The Cl atom lone pairs of electrons can form π molecular orbitals with d_{xz} and d_{yz} . These metal atomic orbitals are π -antibonding MOs in $[CoCl(NH_3)_5]^{2+2}$ (they are nonbonding in $[Co(NH_3)_6]^{3+}$), and so they will be raised in energy relative to their position in $[Co(NH_3)_6]^{3+}$, in which they were degenerate with d_{xy} . Since Cl⁻ ion is not as strong a σ -base as NH₃ is, the d_z^2 orbital in $[CoCl(NH_3)_5]^{2+2}$ will be at lower energy than in $[Co(NH_3)_6]^{3+}$, in which it was degenerate with d_x^2 -y². A qualitative *d*-orbital splitting diagram for both complexes is shown below (L = NH₃).



19.25 Show that the purple color of MnO_4^- cannot arise from a ligand field transition? As discussed in Section 19.5, *Charge-transfer bands*, ligand field transitions can occur for *d*-block metal ions with one or more, but fewer than ten, electrons in the metal *e* and t_2 orbitals. However, the oxidation state of manganese in permanganate anion is Mn(VII), which is d^0 . Therefore, no ligand field transitions are possible. The metal *e* orbitals are the LUMOs, and can act as acceptor orbitals for LMCT transitions. These fully allowed transitions give permanganate its characteristic *intense* purple color.

9.3
$$D_{4h} = S = A_{1g}$$

 $P = E_U, A_{2U}$
 $d = E_g, A_{1g}, B_{1g}, B_{2g}$
 $K = \int_{Z_{X_1y_Z}} \int_{Z_2y_Z} \int_{X_2y_Z} \int_{X_2y_$



* your starting energies (M&L) should be all relative to each other. The middle can be scrambled a bit since you are guessing. This is the actual calculated diagram. 19.8 In case a) the Lumo is lyand centered while the HOMO is Metal centered b) has equal contribution of both. There will be more charge movement in case a) thus it will be more sensitive to solvent. For back bonding we see b) get more since the bonding is more like it than a).

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