

Chapter 19

INTRODUCTION TO TRANSITION METAL COMPLEXES

Exercises

- 19.2 (a) Number of molecules or ions to which a transition ion is bonded.
(b) Ligand that occupies more than one coordination site.
(c) Strong complexing ability of chelates resulting primarily from the entropy increase of the chelation process.
- 19.4 Fluoride ion is one of the few ligands that stabilizes high oxidation states.
- 19.6 (a) Optical isomer; (b) geometric isomer.
- 19.8 (a) Pentacarbonyliron(0); (b) potassium hexafluorocobaltate(III);
(c) hexaaquairon(II) chloride; (d) pentaamminechlorocobalt(III) sulfate.
- 19.10 (a) $[\text{Cr}(\text{NH}_3)_6]\text{Br}_3$; (b) $[\text{Co}(\text{OH}_2)(\text{en})_2(\text{SCN})](\text{NO}_3)_2$; (c) $\text{K}_2[\text{Ni}(\text{CN})_4]$;
(d) $[\text{Co}(\text{en})_3]\text{I}_3$.
- 19.12 (a) *Cis*-dichlorotetraamminechromium(II).
(b) *Fac*-trichlorotriamminechromium(III).
- 19.14 The hexacyanoferrate(III) ion is likely to be low spin, as the cyanide ligand is high in the spectrochemical series and hence produces a large Δ_{oct} . The tetrachloroferrate(III) ion would be high spin, as chloride is low in the spectrochemical series and Δ_{tet} is only about four-ninths of Δ_{oct} .
- 19.16 The smallest value is for chromium(III) with the fluoride ligand that is very low in the spectrochemical series. The next is for chromium(III) with a slightly stronger ligand—water. Then there is chromium(IV) with the fluoride ligand, where an increase in oxidation state leads to an increase in Δ_{oct} . Finally, the largest Δ_{oct} is for chromium(III) with one of the highest ligands in the spectrochemical series—cyanide.

19.18	Configuration	u.p.e.	
	d^1		1
	d^2		2
	d^3		3 (hs), 1 (ls)
	d^4		4 (hs), 0 (ls)
	d^5		5 (hs), 1 (ls)
	d^6		4 (hs), 2 (ls)
	d^7		3
	d^8		2
	d^9		1

19.20 The mixed metal oxide NiFe_2O_4 will adopt the inverse spinel structure, $(\text{Fe}^{3+})_t(\text{Ni}^{2+}, \text{Fe}^{3+})_o\text{O}_4$ as the Fe^{3+} ion has a zero CFSE, hence the optimum situation energetically is for the Ni^{2+} ion to occupy the octahedral sites with Δ_{oct} rather than the tetrahedral sites with $4/9\Delta_{\text{oct}}$.

19.22 Six nitrogen-donor atoms will give a stronger field (larger splitting) than four nitrogen- and two oxygen-donor atoms. The greater splitting for the former is enough to overcome the pairing energy.

Beyond the Basics

19.24 The large cation will tend to stabilize the larger pentachloro-complex. In addition, the cation and anion charges will match, enabling the formation of a simple alternating anion-cation lattice such as the sodium chloride lattice. The name will be hexaamminecobalt(III) pentachlorocuprate(II).

19.26 If the nickel complex is paramagnetic, then it has tetrahedral stereochemistry and only the one form. The diamagnetic palladium analog would be square-planar and have two geometric isomers—*cis* and *trans*.

19.28 The diiodoaurate(II) ion should be the most stable as it involves a soft acid/soft base combination.

19.30 These ligands will complex any trace toxic metal ions that leach from the can walls. As firmly complexed ions, their toxicity will be substantially diminished. The complexed ions will be excreted rather than absorbed.

- 19.32 In its normal oxidation state of +1, silver has a complete d^{10} configuration; thus it is acting as a main group metal. Only in its rare higher oxidation states of +2 and +3 does it have less than a filled d -set. For “normal” chemistry it is probably more useful to consider silver as a main group metal.
- 19.34 For iron, the reduction is a conversion from a d^5 to a d^6 configuration. The addition of an electron to a half-filled d set is energetically less favorable because spin pairing will have to occur. For manganese, the reduction is a conversion from a d^4 to a d^5 configuration. This will give the added stabilization of the half-filled d set.

