## CHAPTER 18

1. What is a complex ion? What is a coordination compound?

*A complex ion is a metal ion with one or more attached ligands. A coordination compound is a compound which contains a complex ion.*

2. What kinds of molecules can serve as ligands?

*Any molecule with an unshared electron pair, usually on oxygen or nitrogen*

3. Suggest an explanation for the fact that ammonia is a very good ligand but the ammonium ion is unable to serve as a ligand.

*The ammonium ion does not have an unshared electron pair on the nitrogen atom.*

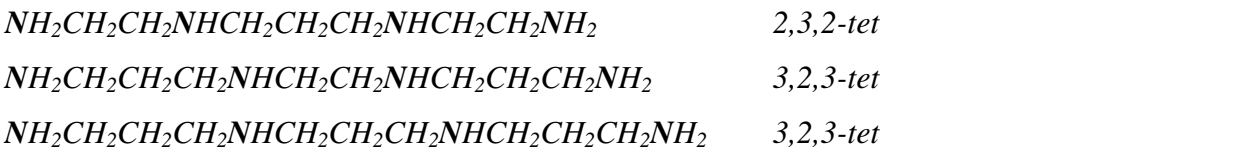
4. Describe each of the following ligands as bidentate, tridentate, tetradentate, and so forth.

| | |
|---|---|
| (a) Ethylenediamine (en) | *bidentate* |
| (b) Diethylenetriamine (dien) | *tridentate* |
| (c) Triethylenetetramine (trien) | *tetradentate* |
| (d) 2,2-bipyridine | *bidentate* |
| (e) 1,10-phenanthroline | *bidentate* |
| (f) ethylenediamine diacetate | *tetradentate* |
| (g) ethylenediamine tetraacetate | *hexadentate* |

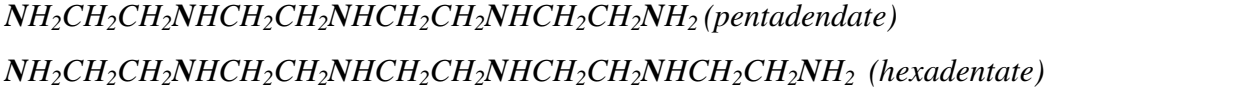
5. What is an ambidentate ligand? Give an example of an ambidentate ligand.

*An ambidentate ligand has two different modes of attachment. Examples include $NO_2^-$ (N or O), $CN^-$ (C or N), and $SCN^-$ (S or N).*

6. Triethylenetetramine is sometimes given the name 2,2,2-tet, where the numbers refer to the number of carbon atoms in the chains joining the nitrogen atoms. Suggest possible structures for 2,3,2-tet, 3,2,3-tet, and 3,3,3-tet.




7. Suggest possible formulas or structures for tetraethylenepentamine and pentaethylenehexamine. How many donor atoms would these ligands have?



8. What is the oxidation state of the transition metal ion in each of the following complexes?

| | | | |
|---|---|---|---|
| (a) $K_4[Fe(CN)_6]$ | $Fe^{+2}$ | (f) $K_4[PtCl_6]$ | $Pt^{+4}$ |
| (b) $K_3[Cr(C_2O_4)_3]$ | $Cr^{+3}$ | (g) $K_2[Ni(CN)_4]$ | $Ni^{+2}$ |
| (c) $[Co(NH_3)_4Cl_2]Cl$ | $Co^{+3}$ | (h) $K_4[Mn(CO_3)_3]$ | $Mn^{+2}$ |
| (d) $[Pt(NH_3)_4]Cl_2$ | $Pt^{2+}$ | (i) $K_3[FeF_6]$ | $Fe^{+3}$ |
| (e) $K_4[Fe(CN)_3Cl_3]$ | $Fe^{+2}$ | (j) $[Pt(NH_3)_6]Cl_4$ | $Pt^{+4}$ |

9. Provide a name for each of the following coordination compounds.

| | |
|---|---|
| (a) $[Cr(NH_3)_6](NO_3)_2$ | *hexaamminechromium(III) nitrate* |
| (b) $Na_3[Cr(NO_2)_6]$ | *sodium hexanitrochromate(III)* |
| (c) $K_3[Co(CO_3)_3]$ | *potassium tris(carbonato)cobaltate(III)* |
| (d) $(NH_4)_4[Fe(C_2O_4)_3]$ | *ammonium tris(oxalato)ferrate(II)* |
| (e) $[Ni(CO)_4](NO_3)$ | *tetracarbonylnickel(II) nitrate* |
| (f) $[Pt(NH_3)_4Cl_2]Br_2$ | *dichlorotetraammineplatinum(II) bromide* |
| (g) $K_2[Cu(NO_2)_4]$ | *potassium tetranitrocuprate(II)* |
| (h) $K[Co(CN)_2(NO_2)_2(NH_3)_2]$ | *potassium dicyanodinitrodiamminecobaltate(III)* |
| (i) $K_4[PtCl_6]$ | *potassium hexachloroplatinate(II)* |
| (j) $K_3[Co(CN)_6]$ | *potassium hexacyanocobaltate(III)* |

10. In some cases both the positive and negative portions of a compound may be complex ions, as in the following examples. Give names for each of the following compounds. Hint: both of these compounds contain Pt in the +2 oxidation state.

| | |
|---|---|
| (a)$[Pt(NH_3)_4][PtCl_4]$ | *tetraammineplatinum(II) tetrachloroplatinate(II)* |
| (b) $[Pt(NH_3)_3Cl]_2[PtCl_4]$ | *chlorotriammineplatinum(II) tetrachloroplatinate(II)* |

11. Provide a formula for each of the following.

| | |
|---|---|
| (a) hexaamminechromium(III) nitrate | $[Cr(NH_3)_6](NO_3)_3$ |
| (b) tetraamminecarbonatocobalt(III) sulfate | $[Co(CO_3)(NH_3)_4]_2SO_4$ |
| (c) sodium tetrabromo(ethylenediamine)cobaltate(III) | $Na[CoBr_4(en)]$ |
| (d) potassium tris(oxalato)chromate(III) | $K_3[Cr(C_2O_4)_3]$ |
| (e) sodium hexanitroferrate(III) | $Na_3[Fe(NO_2)_6]$ |
| (f) hexacarbonylchromium(III) chloride | $[Cr(CO)_6]Cl_3$ |
| (g) ammonium tris(carbonato)chromate(III) | $(NH_4)_3[Cr(CO_3)_3]$ |

12. Using only $NH_3$ and $NO_2^-$ as ligands, give the formula for an octahedral coordination compound containing $Co^{3+}$ that would (a) that would give two ions when dissolved in water, (b) that would give three ions when dissolved in water, and (c) that would give four ions when dissolved in water.

*(a)* $[Cr(NH_3)_4(NO_2)_2]NO_2$

*(b)* $[Cr(NH_3)_5NO_2](NO_2)_2$

*(c)* $[Cr(NH_3)_6](NO_2)_3$

13. Explain why two geometric isomers are possible for $[Co(NH_3)_2Cl_4]^-$ but only one isomer is possible for $[Co(NH_2CH_2CH_2NH_2)Cl_4]^-$.

*To form a trans isomer the ethylenediamine would have to bind to opposite sites (180 degrees apart)*

14. Give the formulas for all possible ionization isomers of each of the following:

(a) $[Co(NH_3)_4(Cl)(NO_2)]CN$

*$[Co(NH_3)_4(CN)(NO_2)]Cl$*

*$[Co(NH_3)_4(Cl)(CN)]NO_2$*

(b) $[Co(en)(CN)_2(NH_3)_2]Cl$

*$[Co(en)(Cl)(CN)(NH_3)_2]CN$*

(c) $[Co(C_2O_4)(NH_3)_4]Cl$

*No other isomers possible*

(d) $[Pt(NH_3)_4Cl_2]Br_2$

*$[Pt(NH_3)_4ClBr]BrCl$*

*$[Pt(NH_3)_4Br_2]Cl_2$*

15. Sketch all possible geometric isomers for each of the following compounds:

(a) $[Co(NO_2)_3Cl_3]^{3-}$ (two geometric isomers)

(b) $[Co(dien)Cl_3]$ (two geometric isomers)

(c) $[Co(NH_3)_2(Br)_2(Cl_2)]^-$ (five geometric and one optical isomers)

(d) $[Co(en)(C_2O_4)Cl_2]^+$

(e) $[Co(dien)(en)Cl]^{2+}$

(f) $[Co(en)(C_2O_4)(Cl)(NH_3)]^{2+}$

16. Consider the structure of the porphyrin molecule. Sketch at least one other resonance structure for this molecule.

17. What is a chelating ligand? What is the chelate effect?

*A chelate ligand is any ligand with two or more donor atoms. The chelate effect is the tendency of compounds with chelate ligands to have larger formation constants.*

18. Which do you think would have a larger formation constant, $[Co(en)_3]^{2+}$ or $[Co(dien)_2]^{3+}$? (en = ethylenediamine, dien = diethylenetriamine). Why?

*The diethyleneteiamine compound would have the greater formation constant, because it is tridentate and each could replace three monodentate ligands.*

19. Explain why $NO_2^-$ is able to function as an ambidentate ligand but the $NO_3^-$ is not. (You may wish to draw Lewis structures for these two molecules before attempting to answer this question.)

*The nitrogen atom in the $NO_3^-$ ion does not have any unshared pairs and as a result is unable to coordinate.*

20. The oxalate ($C_2O_4^{2-}$) ion is a common bidentate ligand. Draw all possible resonance structures for this ion, including formal charges. Do you think that this ion will likely bind through two oxygen atoms on the same carbon or through two oxygen atoms on two different carbon atoms? Explain your answer.

21. Explain why the $Co^{2+}$ ion is considered to be "softer" than the $Co^{3+}$ ion.

*As successive electrons are removed, an atom becomes smaller; $Co^{3+}$ is smaller than $Co^{+2}$ and is therefore less easily deformed.*

22. Of the five types of isomers discussed (geometric isomers, optical isomers, ionization isomers, linkage isomers, coordination isomers), which are constitutional isomers? Which are stereoisomers?

*Stereoisomers – geometric isomers, optical isomers*
*Constitutional isomers – ionization isomers, linkage isomers, coordination isomers*

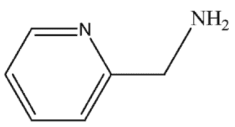
23. Determine the formulas for all possible coordination isomers of the compound $[Co(NH_3)_6][Cr(NO_2)_6]$.

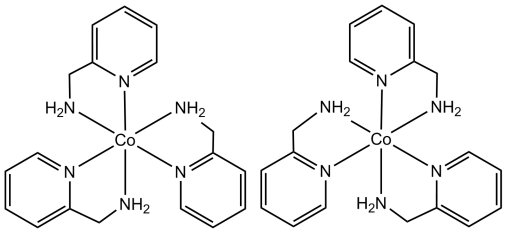
*$[Co(NH_3)_5(NO_2)][Cr(NO_2)_5(NH_3)]$*
*$[Co(NH_3)_4(NO_2)_2][Cr(NO_2)_4(NH_3)_2]$*
*$[Cr(NH_3)_5(NO_2)][Co(NO_2)_5(NH_3)]$*
*$[Cr(NH_3)_4(NO_2)_2][Co(NO_2)_4(NH_3)_2]$*

*The compound $[Co(NH_3)_3(NO_2)_3][Cr(NO_2)_3(NH_3)_3]$ is also possible, however +3 is the most common oxidation state for Cr and Co, and so no charges would be present (and therefore no interaction between the two)*

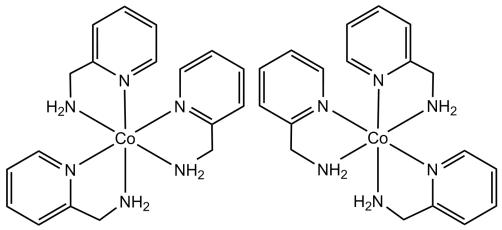
24. The tripodal ligand $N(CH_2CH_2NH_2)_3$ coordinates to form a single isomer. Suppose that one of the ethylene linkages is replaced with a propylene linkage, giving the formula $N(CH_2CH_2NH_2)_2(CH_2CH_2CH_2NH_2)$. Coordination of the modified ligand to an octahedral metal ion gives two different isomers. Sketch these two isomers.

25. Consider the asymmetric bidentate ligand 2-(aminomethyl)pyridine (*ampy*) which has the structure shown to the right. How many isomers (including both geometric and optical isomers) are possible for the complex ion $[Co(ampy)_3]^{3+}$? Sketch these isomers.



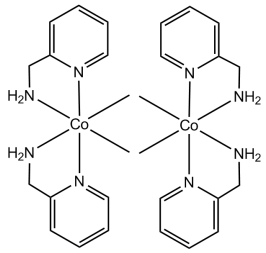


facial (enantiomers)

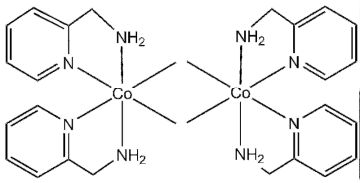


meridional (enantiomers)

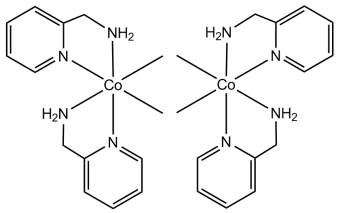
26. How many isomers (including both geometric and optical isomers) are possible for the compound $[Co(ampy)_2(NH_3)_2]^{3+}$? Sketch these isomers.



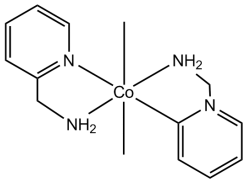
s-cis (enantiomers)



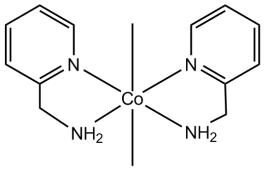
s-cis (enantiomers)



u-cis (enantiomers)

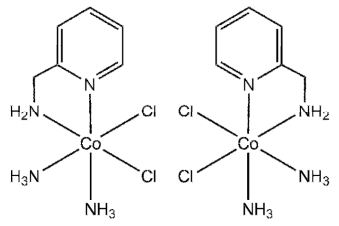


trans

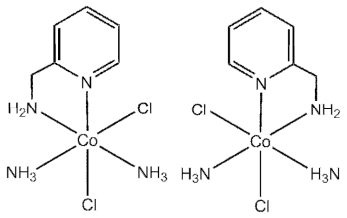


trans

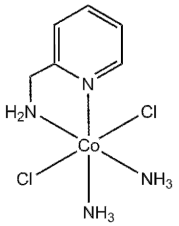
27. How many isomers (including both geometric and optical isomers) are possible for the compound $[Co(ampy)(NH_3)_2Cl_2]^+$? Sketch these isomers.



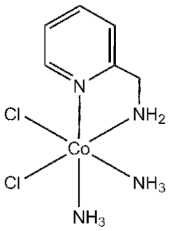
enantiomers



enantiomers

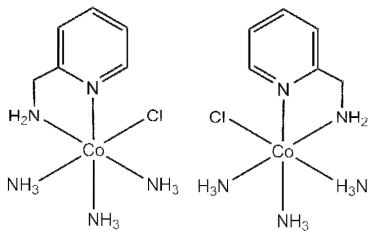


Cl trans

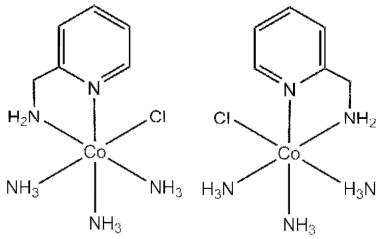


$NH_3$ trans

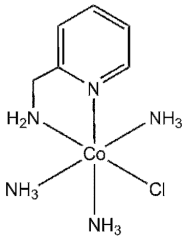
28. How many isomers (including both geometric and optical isomers) are possible for the compound $[Co(ampy)(NH_3)_3Cl]^{2+}$? Sketch these isomers.



Enantiomers



Cl *trans* to pyridine N



Cl *trans* to $NH_2$

29. Sketch two mirror images of the *symmetrical-cis* $[Co(trien)Cl_2]^+$ ion.

30. Sketch two mirror images of the *unsymmetrical-cis* $[Co(trien)Cl_2]^+$ ion.

31. Suppose that one of the N-donor atoms in triethylenetetramine were replaced with a sulfur atom, giving the ligand $NH_2CH_2CH_2NHCH_2CH_2SCH_2CH_2NH_2$, which will henceforth be abbreviated NNSN. Sketch all possible isomers for the $[Co(NNSN)]^{3+}$ ion.