CHEM1102 Worksheet 12: Coordination Chemistry

Model 1: The oxidation number and electronic configuration of transition metal cations in coordination compounds

The sum of the charges of the metal cation and its ligands adds up to give the charge of the complex ion. If the complex ion is charged, this is balanced by counter ions.

The number of valence electrons on an atom is equal to its group number. In a cation, the oxidation number is equal to the number of these electrons which have been removed. Transition metal cations have a configuration d^z where z is the number of valence electrons *left over after ionization*:

> **z = number of valence electrons on atom – charge of cation**
> **= group number – oxidation number**

For example:
(a) Ni is in group 10 so Ni^{2+} has (10 – 2) = 8 valence electrons left: it has a d^8 configuration.
(b) Cr is in group 6 so Cr^{3+} has (6 – 3) = 3 valence electrons left: it has a d^3 configuration.

Critical thinking questions

1. Complete the 'oxidation number' column of the table below by working out the oxidation number of each of the transition metal cations.
2. Complete the '*d* configuration' column in the table by working out z for each of the transition metal ions.

Model 2: To minimize repulsion, electrons occupy orbitals singly before they pair up

There are five *d*-orbitals and, as each orbital can accommodate two electrons, there is space for a maximum of ten electrons The electrons are added to these orbitals using Model 2. This has been completed for the complexes in the first three rows of the table.

If this process leads to unpaired electrons, the complex is *paramagnetic* and is attracted towards magnetic field. If there are no unpaired electrons, the complex is *diamagnetic* and is repelled by magnets.

Critical thinking questions

1. Show the electron configuration for the transition metal cation using the box notation in the table.
2. Indicate if the complex is paramagnetic or not in the final column of the table.

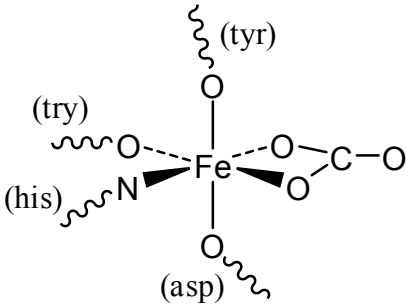
Coordination Compound or Complex	Oxidation Number	*d* Configuration	Electron Arrangement	Paramagnetic?
$K_2[NiCl_4]$	+2	d^8	↑↓ ↑↓ ↑↓ ↑ ↑	Yes
$[Cr(en)_3]Br_3$	+3	d^3	↑ ↑ ↑	Yes
$Na[MnO_4]$				

$(NH_4)_2[CoCl_4]$								
$[Cr(NH_3)_5(H_2O)]Cl_3$								
$[Zn(en)_2Cl_2]$								

*en is $NH_2CH_2CH_2NH_2$ and can bond through lone pairs on *both* N atoms.

Model 3: Iron in Biology (1): Transferrin

Iron is found in many biological molecules. Typical of its coordination chemistry in fairly recently evolved systems is *transferrin*, which is used to transport iron in the blood. The Fe(III) atom is bonded to O and N atoms through five ligands: 4 amino acids and 1 carbonate anion (CO_3^{2-}).



Critical thinking questions

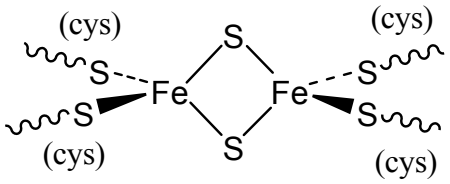
1. How many unpaired electrons will the Fe(III) atom have?

2. What is the coordination number and approximate geometry of the Fe(III) atom. Describe how this is achieved with 5 ligands.

3. The Fe(III) is released in a cell by a decrease in the pH. Use your knowledge of acid-base chemistry to suggest what the effect of low pH will be on the ligands in the complex.

Model 4: Iron in Biology (2): Ferredoxins

Iron-sulfur clusters are widespread in biology and date further back in evolutionary time. They contain Fe(II) and/or Fe(III) ions coordinated by S atoms, the simplest of which is shown opposite. They are involved in redox reactions in which the oxidation numbers of the iron atoms change.



Critical thinking questions

1. What are the coordination numbers and approximate geometries of the Fe atoms?

2. How many unpaired electrons will a Fe(II) atom and a Fe(III) atom have?

3. Given your answer to Q2, suggest why magnetic studies indicate no *net* unpaired electrons when both iron atoms are present as Fe(III) in this cluster.

4. Using your answer to Q3, predict the *net* number of unpaired electrons in the reduced form containing one Fe(II) and one Fe(III).