Summary of Coordination Compounds

History:

Alfred Werner won the Nobel Prize in chemistry in 1913 for proposing octahedral configurations of transition metal complexes. He also defined the terms Coordination Number and oxidation number of metal based on the nature of valency.

Definitions:

A coordination complex is the product of a Lewis acid-base reaction in which neutral molecules or anions (called ligands) bond to a central metal atom or ion by coordinate covalent bonds.

The Coordination Number (CN) is the number of donor atoms bonded directly to the central metal atom.

Ligands which donate a single pair of electrons to a central metal atom are called monodentate, if they donate two pairs of electrons they are called bidentate and if they donate more than two pairs of electrons they are called polydentate ligands. Bidentate ligands are also called chelating ligands. Complex that contain chelating ligands are called chelate.

Complexes that contain polydentate ligands are more stable because:
- the entropy increases by forming the complex
- five or six membered rings are formed
- the probability of breaking all bonds of a polydentate ligand is within a time-window is low

Ambidentate ligands have more than one potential donor atom, e.g. NO_2. If the nitrogen atom of NO_2 attaches to the metal, the ligand is called "nitro" and if oxygen of the NO_2 group attaches to the metal, the ligand is called "nitrito".
Examples: F^-, H_2O, NH_3, CN^-, CO (Monodentate), NH_2-CH-CH-NH_2 (Bidentate), EDTA (Poly-dentate).
The sodium salt of EDTA can be found in many commercial products including soap, beer and mayonnaise.

Constitution and Geometry:

The most important factors that govern the CN of a complex are
1) The size of the central metal atom or ion.
2) The steric interaction between ligands.
3) Electronic interactions between the central atom or ion and the ligands.

Based on above mentioned factors bulky ligands result in low CN's. Higher CN's are most common on the left of a period and lower CN's are found on the right of the d-block.
e.g.: $[Mo(CN)_8]^{4-}$ has high CN and $[PtCl_4]^{2-}$ has low CN

Complexes with CN = 2: These are found for Cu^+ and Ag^+. Examples are $[AgCl_2]^-$ and $HgMe_2$. The geometry is linear.

Complexes with CN = 3: These are very rare among metal complexes, but are found with bulky ligands.
e.g.: $[Pt(PCY_3)_3]$ tricyclohexylphosphine. The ligands are in trigonal arrangement.

Complexes with CN = 4: Tetrahedral complexes are favored over higher coordinated complexes if the central atom is small or the ligands are large. Square planar complexes are typically observed for metals with d^8 configuration.
Four coordinated S and P- block complexes without lone pair on the central atom, such as $[BeCl_4]^{2-}$ or $[BF_4]^-$ are always tetrahedral.

Complexes with CN = 5: Square pyramidal five coordinated complex are found in the biologically porphyrins.
Another possible geometry for CN 5 is trigonal bipyramidal.

Complexes with CN = 6: The majority of six coordinated complexes are octahedral. A coordination number of 6 is found for s, p, d and f metal coordination compounds. The deviations from octahedra symmetry are tetragonal, rhombic, and trigonal distortions.

Higher CN´s: Large atoms particularly those of the f-block tend to form complexes with high CN´s. Seven coordinated complexes are encountered in a few 3d complexes and many more 4d and 5d complexes. The geometries are pentagonal bipyramidal, capped octahedral, capped trigonal prismatic.
Relatively large ions can act as host for nine coordinated complexes. e.g.: $[Nd(OH_2)_9]^{3+}$

Questions:
1) Define basic terms in coordination compounds. Explain the factors affecting the stability of chelate complexes.
2) What are the factors influencing the geometry of a complex? For which electronic configuration a square planar coordination is typical. Give an example.