Some special type of ligands

Give examples of bridging ligand chelating ligand and flexidentate ligand.

(i) Bridging Ligands:

A monodentate ligand may have more than one free electron pairs and thus may simultaneously co-ordinate with two or more atoms i.e; the ligand forms two sigma bonds with two metal atoms and thus acts as a bridge betn the metal atoms. Such a ligand is called a bridging ligand and the resulting complex is known as bridged complex.

e.g; $OH^{\ominus}$, $F^{\ominus}$, $Cl^{\ominus}$, $NH_2^{\ominus}$, CO, O^{2-}, $SO_4^{=}$ etc.

(ii) Symmetrical and unsymmetrical bidentate ligands

Bi-dentate ligands may be symmetrical or unsymmetrical; in symmetrical bidentate ligands, the two co-ordinating atoms are the same while in unsymmetrical bidentate ligands, the co-ordinating atoms are different. Thus symmetrical and unsymmetrical bidentate ligands are generally represented as (AA) and (AB) respectively where 'A' and 'B' are the donor atoms.

e.g; Symmetrical: (i) en (ethylene di-amine) ($NH_2-CH_2-CH_2-NH_2$)

(ii) ox (oxalate) iii) EAA (iv) bpy v) DMG

Unsymmetrical: gly ($CH_2<^{COO^{\ominus}}_{NH_2}$). glycene ($CH_2<^{COOH}_{NH_2}$)

(iii) Ambidentate ligands:

Give examples of an ambidentate ligand and draw the strs. of its complexes showing ambidentate nature.

There are many ligands which have two or more different donor atoms in their structure. Such ligands can co-ordinate to the metal atoms through any of their donor atoms and hence are given different names corresponding to the nature of donor atoms linked to the metal atom. Such ligands are called ambidentate ligands.

Q. How would you show that SCN- acts as an ambidentate ligand?

e.g.; Ligands → complexes

(i) $[O-N=O]^{\ominus}$ ion → { M−NO₂ (nitro); M−O−N=O (nitrito) }

(ii) $[C\equiv N]^{\ominus}$ ion → { M−C≡N (cyano); M−N≡C (isocyano) }

(iii) $[S-C\equiv N]^{\ominus}$ ion → { M−S−C≡N (thiocyanato); $M-\overset{\oplus}{N}\equiv C-S^{\ominus}$ (isothiocyanato) }

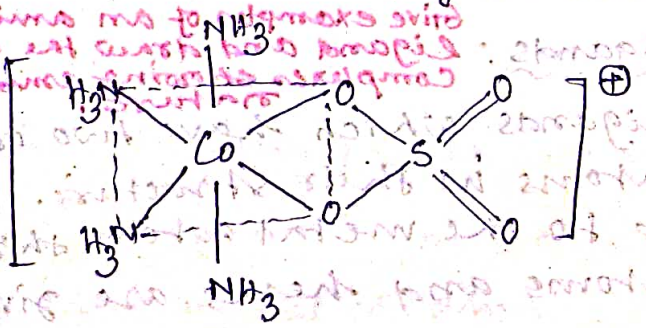
(iv) Flexidentate ligands: (examples) & Definition

Some bidentate or polydentate ligands have flexidentate character i.e; a bidentate or polydentate ligand may not necessarily used all its donor atoms to get co-ordinated to the metal ion.

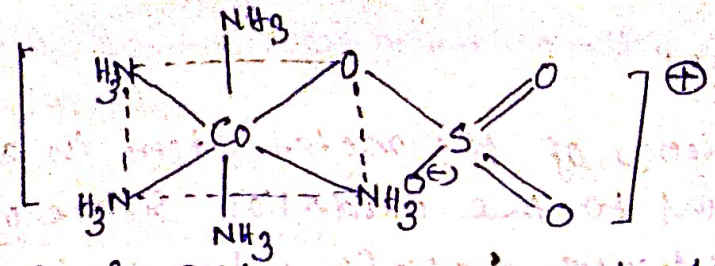
Such type of ligands are called flexidentate ligands. e.g.; $SO_3^{=}$, $CO_3^{=}$, N_2 etc have two donor atoms. When these ligands get co-ordinated to the metal atom or ion, they give rise to the formation of two types of complex-compounds.

In one type they get linked to the metal atom through one donor atom only while in the formation of another type of the complex compound, they get co-ordinated to the metal atom through both of its donor atoms.

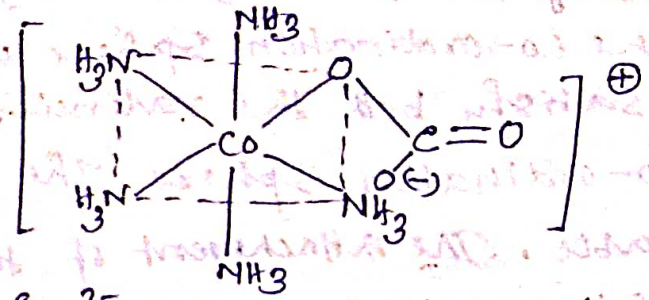
These are shown in figure below;



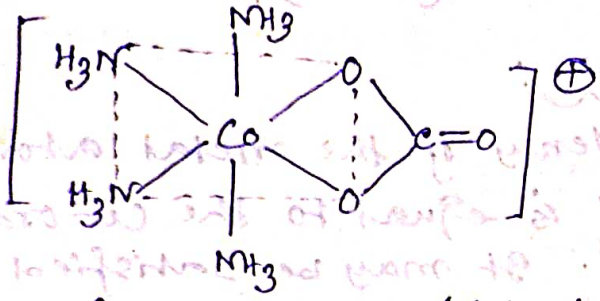
fig; SO_3^{2-} acts as a bidentate ligands.



fig; SO_4^{2-} acts as a monodentate ligand.



fig; CO_3^{2-} acts as a monodentate ligand.



fig; CO_3^{2-} acts as a bidentate ligand.

Ethylene di-amine tetra acetic acid which usually acts as a hexadentate ligand functions as a pentadentate ligand in $[Cr(OH)(HEDTA)]^{\ominus}$ and as a tetradentate ligand in $[Pd(H_2EDTA)]^{0}$.

Hence these polydentate ligand behaves as a flexidentate ligand.

Q. Give example of one type of interaction that could not be accounted by Werner's theory.

② Werner's Co-ordination Theory :

To explain the observed properties of complex comps. Werner proposed a theory known as Werner's Co-ordination theory.

Different postulates of Werner's Co-ordination theory

① In complex compound, the central metal atom exhibits two types of valency—
   (i) primary valency
   (ii) Secondary valency.

The metal atoms always tends to satisfy of its valency.

(i) Primary valency:

The primary valency of the metal atom in a complex compound is equal to the oxidation state of the metal. It is always satisfied by anions. The anions satisfying the primary valency are written outside the co-ordination sphere while the anions which satisfy both the valencies are written inside co-ordination sphere. The primary valency is ionisable. The attachment of the species satisfying the primary valency to the metal is shown by broken line (- - - -).

(ii) Secondary valency:

The secondary valency of the metal atom in a complex compound is equal to the co-ordination no. of that metal. It may be satisfied by anions, cations as well as neutral molecules. The species satisfying the secondary valency are called ligands while writing the structure of a complex compound. The species satisfying the secondary valency and the metal are written in side the co-ordination sphere. It is also called non-ionisable valency. Because the species satisfying the secondary valency are not ionisable. The attachment of the species satisfying the secondary valency with the metal atom is shown by a solid line (—).

(2) Generally the central metal ion exhibits a constant co-ordination no.

e.g:

Metal ion	Co-ordination no (c.N)
Co^{3+}, Cr^{3+}, Fe^{3+}, Fe^{2+}, Pt^{4+}	6
Co^{2+}, Pt^{2+}, Cd^{2+}, Cu^{2+}	4
Ag^{+}, Ag_2^{2+}	2