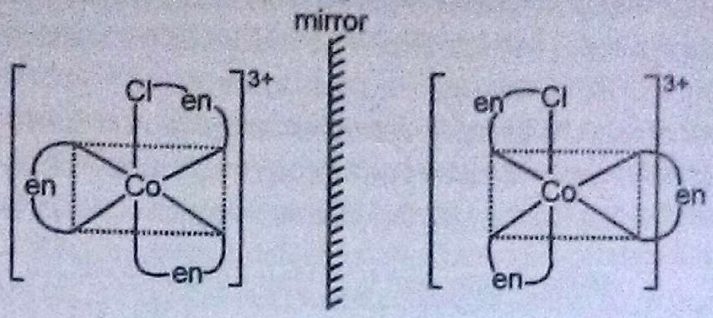
(v) Optical isomers of $[Co(en)_3]^{3+}$ are



BONDING IN COMPLEXES

Werner's Co-ordination Theory :

Alfred Werner put forward his concept of secondary valency for advancing a correct explanation for the characteristics of the co-ordination compounds. The fundamental postulates of Werner's theory are as follows.

(i) Metals possess two types of valencies, namely, primary (principal or ionisable) valency and secondary (auxillary or non-ioisable) valency.

In modern terminology, the primary valency corresponds to oxidation number and secondary valency to co-ordination number. According to werner primary valencies are shown by dotted lines and secondary valencies by thick lines.

(ii) Every metal cation in complex compound has a fixed number of secondary valencies for example Pt^{4+} cation has its six secondary valency.

(iii) Primary valency is satisfied by negative ions, whereas secondary valency is satisfied either by negative ions or by neutral molecules.

(iv) Primary valency has non-directional character, where as secondary valency has directional character, therefore a complex ion has its definite geometry eg. $[Co(NH_3)_6]^{3+}$ – octahedral.

(v) It is the directional nature of secondary valency due to which co-ordination compound exhibits the phenomenon of isomerism.

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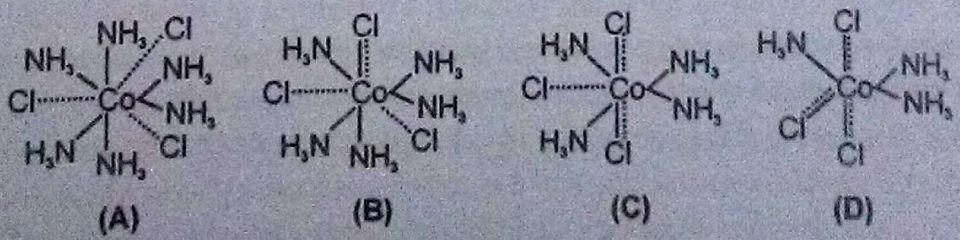
Werner's Representation of Complexes

Consider the case of $CoCl_3.xNH_3$ where primary valency = +3 and secondary valency = 6.

Various structures are summarised in Table 4.

	Werner complexes	*Modern formula*	*Ionisation*	*Secondary valency satisfied by*	*Primary valency staisfied by*
(A)	$CoCl_3.6NH_3$	$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]^{3+} + 3Cl^-$	six (NH_3)	three (Cl^-)
(B)	$CoCl_3.5\ NH_3$	$[Co(NH_3)_5Cl]Cl_2$	$[Co(NH_3)_5Cl]^{2+} + 2Cl^-$	five (NH_3) and one (Cl^-)	three (Cl^-) including one (Cl^-) with dual nature
(C)	$CoCl_3.4\ NH_3$	$[Co(NH_3)_4\ Cl_2]Cl$	$[Co(NH_3)_4Cl_2]^+ + Cl^-$	four (NH_3) and two (Cl^-)	three (Cl^-) including two (Cl^-) with dual nature
(D)	$CoCl.3NH_3$	$[Co(NH_3)_3Cl_3]$	$[Co(NH_3)_3]Cl_3$	three (NH_3) and three (Cl^-)	three (Cl^-) all with dual nature

- From Table 4, it is clear that conduction of the complexes will be in the order D < C < B < A.
- They are represented as



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According to C.F.T. Splitting of d-orbitals in various ligand fields

Δ_t = Crystal Field Stablization Energy (CFSE) for tetrahedral complex

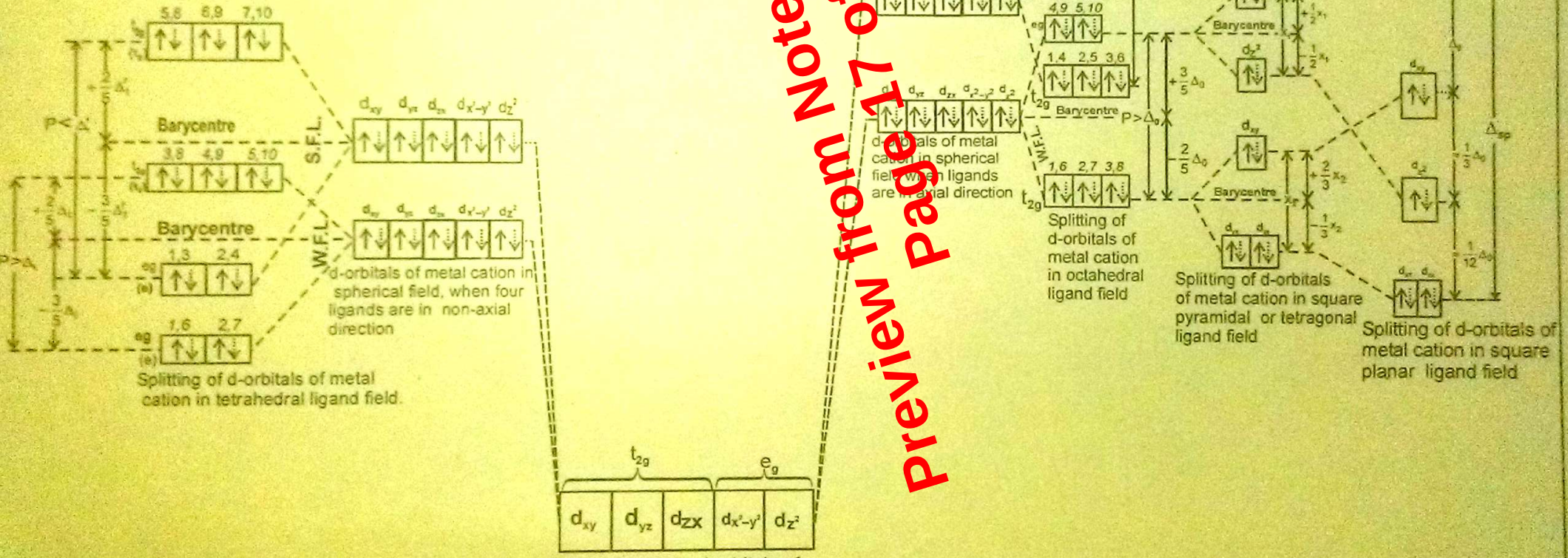
$$\Delta_t = -\frac{4}{9}\Delta_o$$

Δ_o = Crystal Field Stablization Energy (CFSE) for octahedral complex

Δ_{sp} = Crystal Field Stablization Energy (CFSE) for square planar complex

$\Delta_o = 10\ Dq$ $\quad$ $\Delta_{sp} = 1.3\ \Delta_o$

Energy



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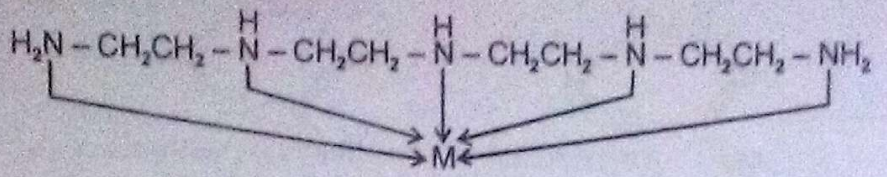
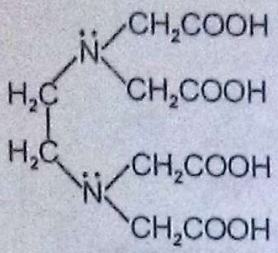
(d) **Pentadentate ligand :**



tetraethylenepentaamine (teten)

(e) **Hexadentate Ligand :**



(H_4EDTA)

$H_4EDTA \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} EDTA^{4-}$

H_4EDTA (water insoluble) Ethylenediaminetetraacetic acid

$EDTA^{4-}$ (water soluble) Ethylenediaminetetraacetate

Flexidentate character of $EDTA^{4-}$

Ligands	Denticity
H_4EDTA	2
H_3EDTA^- [ethylenediamineacetate]	3
H_2EDTA^{2-} [ethylenediaminediacetate]	4
$HEDTA^{3-}$ [ethylenediaminetriacetate]	5
$EDTA^{4-}$	6

As pH of solution decreases denticity of $EDTA^{4-}$ also decreases

* $EDTA^{4-}$ always gives octahedron geometry due to six coordination sites.

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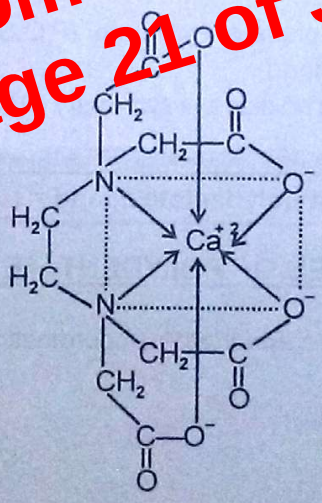
No. of N – Ca – N Bond angles = 1

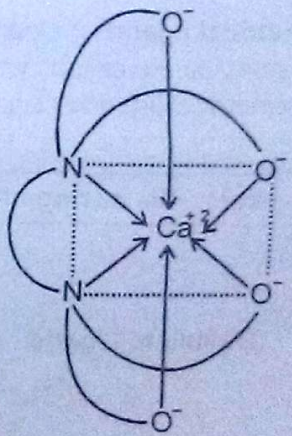
No. of O – Ca – O Bond angles = 6

No. of N – Ca – O Bond angles = 8



$[Ca(EDTA)]^{2-}$

OR



$[Ca(EDTA)]^{2-}$

(III) Ambidentate Ligands : When negative ligands have at least two different donor sites, but at a time of coordination only one donor site is used are called ambidentate ligands with monodentate behaviour. However Ambidentate ligands having sp^2 or sp^3 hybridized central atom, can also act as flexidentate ligands.

$M \leftarrow \underline{S}CN^-$	:	Thiocyanate - S
$M \leftarrow \underline{N}CS^-$	:	Thiocyanate - N
$M \leftarrow \underline{O}CN^-$	:	Cyanate
$M \leftarrow \underline{N}CO^-$	:	Isocyanate
$M \leftarrow \underline{C}N^-$	:	Cyanide
$M \leftarrow \underline{N}C^-$	:	Isocyanide

These ambidentate Ligands always show monodentate behaviour.

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RULES FOR IUPAC NAMING OF COMPLEX COMPOUNDS

1. In IUPAC naming of complex compound positive (cationic) part is named first, whether it is simple or complex followed by naming of negative (anionic) part.

2. In IUPAC naming of complex ion, ligands are named first according to alphabetical order of their names followed by naming of central metal atom / ion.

3. When there are several monodentate ligands of the same type, then prefix di, tri, tetra, penta, hexa etc. are provided to the ligands. If monodentate ligand's name already contain any of these prefix then to avoid confusion, 'bis', 'tris', 'tetrakis' 'pentakis' are used instead of di, tri, tetra, penta etc. and ligand's name is placed in parenthesis. Bis, tris prefix is also provided to chelating ligands forming stable 5/6 membered ring with central metal atom/ion and also with π-acid ligands which can be involved in π-donation with central metal atom/ion.

4. Negative ligands have suffix — o,
Positive ligands have suffix — ium,
Neutral ligands have no specific suffix.

Monodentate ligands : (with their IUPAC names)

$\underline{H}^-$	Hydrido	$CH_3\underline{O}^-$	Methoxo / Methoxido	$\underline{N}^{3-}$	Nitrido
$\underline{F}^-$	Flouro/Flourido	$\underline{O}CN^-$	Cyanato	$\underline{NH_2}^-$	Amido
$\underline{Cl}^-$	Chloro/Chlorido	$\underline{N}CO^-$	Isocyanato	$\underline{NH}^{2-}$	Imido
$\underline{Br}^-$	Bromo/Bromido	$\underline{S}CN^-$	Thiocyanato/Thiocyanato - S	$\underline{NO_2}^-$	Nitro/Nitrito-N
$\underline{I}^-$	Iodo/Iodido	$\underline{N}CS^-$	Isothiocyanato/Thiocyanato-N	$\underline{O}NO^-$	Nitrito/Nitrito-O
$\underline{O}^{2-}$	Oxo/Oxido	$\underline{SO_4}^{2-}$	Sulphato	$\underline{NO_3}^-$	Nitrato
$\underline{O_2}^{2-}$	Peroxo/peroxide	$\underline{SO_3}^{2-}$	Sulphito	$\underline{C}N^-$	Cyano / Cyanido
$\underline{O_2}^-$	Superoxo/Superoxido	$\underline{S_2O_3}^{2-}$	Thiosulphato	$CH_3C\underline{O}O^-$	Acetato
$\underline{O}H^-$	Hydroxo/Hydroxido	$\underline{N_3}^-$	Azido	$\underline{C_2O_4}^{2-}$	Oxalato
				$\underline{CO_3}^{2-}$	Carbonato
				$Sn\underline{Cl_3}^-$	Trichlorostannito

Note : Underlined Atoms are donar site of ligands.

But negative organic ligands having '–yl' suffix of hydrocarbon origin are not replaced by '-o'

CH_3^- – Methyl

$C_2H_5^-$ – Ethyl

– Cyclopentadienyl

5. Usually common names are provided to the neutral ligands
except NH_3(Ammine), H_2O(Aqua/Aquo), CO(Carbonyl), NO(Nitrosyl),

eg. N_2(Dinitrogen), O_2(Dioxygen), PH_3(Phosphene), PMe_3(Trimethyl phosphene), PPh_3(Triphenyl phosphene), N_2H_4(Hydrazine), $MeNH_2$(Methyl amine), $EtNH_2$(Ethyl amine), Me_2O(Dimethyl ether), Me_2S(Dimethyl thioether), C_6H_6(Benzene), C_5H_5N(Pyridine)

6. Oxidation state of central metal atom/ion is represented by roman numerals including zero immediate after metal's name in parenthesis.

7. In IUPAC naming of complex anion, central metal atom has suffix '–ate' along with its english or latin name but in case of complex cation/complex neutral molecule central metal atom has no specific suffix with its name.

Metal in complex anion	– ium → + ate
Cr	Chromate
Pd	Palladate
Os	Osmate
Ir	Iridate

Usually latin names are used for those metals whose symbol is derived from corresponding latin names, Cu (Cuprum); Fe (Ferrum); Ag(Argentum); Na(Natrium); Au(Aurum); K(Kalium); Sn(Stannum); Pb(Plumbum) Except : Hg(Mercury); Sb(Antimony); W(Tungsten).

8. In case of polynuclear/bridging complex compound, μ - prefix is provided to bridging ligand when it is coordinated with two metal atoms/ion. When bridinging ligand is coordinated with more than two metal atoms, then prefix μ_3, μ_4, ...etc. are provided to the bridging ligands.

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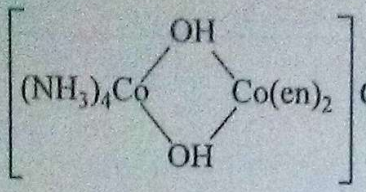
29. $[Pt(NH_3)_4][Cr(NCS)(NO_2)_2(NH_3)_2Py]$ ⟶ Tetrammine platinum (II) diammine dinitrito-N pyridine thiocyanato-N chromate (I)

30. $K_3[Co(C_2O_4)_2Cl_2]$ ⟶ Potassium dichlorobis(oxalato)cobaltate (III)

31.  ⟶ Tetraamine cobalt (III) di–μ–hydroxo bis (ethylenediamine) cobalt (III) chloride {III way is not applicable}

32. $Na_2[Pt(CN)_2I(NO_2)]$ ⟶ Sodium dicyanidoiodidonitrito-N-platinate (II)

33. $[Ru(PPh_3)_3Cl_3]$ ⟶ Trichlorotris(triphenylphosphine)ruthenium(III)

34. $K_2[Co(N_3)_4]$ ⟶ Potassium tetraazidocobaltate (II)

35. $[NiCl_2(Ph_3P)_2]$ ⟶ Dichlorobis(triphenylphosphine) nickel (II)

36. $[Cr(acac)_3]$ ⟶ Tris(acetylacetanato) chromium (III)

37. $[IrCl(CO)(Ph_3P)_2]$ ⟶ Carbonylchlorobis(triphenylphosphine) iridium (I)

38. $[Co(NCS)(NH_3)_5]Cl_2$ ⟶ Pentaammine thiocyanato–N cobalt (III) chloride

39. $[Pt(C_5H_5N)_4][PtCl_4]$ ⟶ Tetrapyridine platinum (II) tetrachloroplatinate (II)

40. $[CrCl(ONO)(NH_3)_4]NO_3$ ⟶ Tetraammine chloronitrito-O-chromium (III) nitrate

41. $[Co(NH_3)_6][CuCl_5]$ ⟶ Hexaamminecobalt (III) pentachlorocuprate (II)

42. $[Ca(EDTA)]^{2-}$ ⟶ Ethylenediaminetetraacetato calcate (II) ion

43. $[Fe(H_2O)_5(NO)]SO_4$ ⟶ Pentaaquanitrosonium iron (I) sulphate [brown ring complex is untable]

44. $K_4[Ni(CN)_4]$ ⟶ Potassium tetracyanidonickelate (O)

45. $[Al(OH)(H_2O)_5]SO_4$ ⟶ Pentaaquohydroxoaluminium (III) sulphate

46. $[VBr_2(H_2O)(NH_3)_2]Br$ ⟶ Diammine aquodibromovanadium (III) bromide

47. $Na[Co(CO)_4]$ ⟶ Sodium tetracarbonylcobaltate (–I)

48. $Fe_4[Fe(CN)_6]_3$ ⟶ Iron (III) hexacyanidoferrate (II)

49. $Fe_3[Fe(CN)_6]_2$ ⟶ Iron (II) hexacyanidoferrate (III)

50. $[Cr(en)_3][Ni(CN)_5]$ ⟶ Tris (ethylenediamine) chromium (III) pentacyanido nickelate (II)

51. $[(NH_3)_4CoNH_2NO_2Co(NH_3)_4](NO_3)_4$ ⟶ μ–amido μ–nitro bis {tetraammine cobalt (III)} nitrate
⟶ Tetraammine cobalt (III) μ–amido μ–nitro tetraammine cobalt (III) nitrate
⟶ μ–amido μ–nitro–octamminedicobalt (III) nitrate

52. $K[B(C_2H_5)_4]$ ⟶ Potassium tetraethyl borate (III)

53. $[PtBr(NH_3)_3]NO_3$ ⟶ Triamminebromoplatinum (II) nitrate

54. trans-$[PtCl_2(NH_3)_2]$ ⟶ Trans–diammine dichloroplatinum (II)

55. $[RhCl(PPh_3)_3]$ ⟶ Chlorotris (triphenylphosphine) rhodium (I)

56. $[Ni(dmg)_2]$ ⟶ Bis (dimethylglyoximato) nickel (II)

57. $[Co(NH_3)_6][Cr(CN)_6]$ ⟶ Hexaamminecobalt (III) hexacyanidochromate (III)

58. $Ni(\pi\text{–}C_4H_4)_2$ ⟶ bis (η^4- cyclobutadiene) nickel (0)

59. $[CoCl(NCS)(NH_3)_4]^+$ ⟶ Tetraamminechlorothiocyanato–N cobalt (III) ion

60. $[PtCl_4(en)]$ ⟶ Tetrachloroethylenediamine platinum (IV)

61. $[CoBrCl(en)(NH_3)_2]NO_3$ ⟶ Diamminebromochloroethylenediamine cobalt (III) nitrate

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