VALANCE BOND THEORY

The application of valence bond theory to complexes is based on three basic assumptions:

1. *The metal-ligand bond is a coordinated covalent bond. Complex formation is considered a Lewis acid-base reaction.*

2. *The empty orbitals prepared by the central atom are not ordinary atomic orbitals, but are the hybrid orbitals formed by the use of s, p, d and f orbitals. The geometry is predicted from hybridization type.*

3. *The electronic structure of the central atom interacting with the ligands may vary. The paramagnetic moment is determined by measuring the magnetic susceptibility and is related to the number of unpaired electrons of the complex.*

$$\mu = \sqrt{n(n+2)}$$

μ=BM (Paramagnetic moment in Bohr magneton)
*n=Number of unpaired electrons*

Valence bond theory was developed in 1931 by Linus Pauling. According to the valence bond theory, the ligands donate a pair of electrons to the central atom as the Lewis base. The central atom, a Lewis acid, contains empty and suitable energy orbitals. As a result, the ligands are complexed by coordinate covalent bonds to the central atom.

Coordination Number	Geometry	Hybridization	Example
2	Linear	sp (s, p_z)	$[Ag(NH_3)_2]^+$
3	Triangle plane	sp^2 (s, p_x, p_y)	$[HgI_3]^-$
4	Tetrahedron	sp^3 (s, p^3)	$[Ni(CO)_4]$
4	Tetrahedron	d^3s $(d_{xy}, d_{xz}, d_{yz}, s)$	$[MnO_4]^-$
4	Square plane	dsp^2 (d_{x2-y2}, s, p_x, p_y)	$[Ni(CN)_4]^{2-}$
5	Triangular bipyrmid	dsp^3 (d_{z2}, s, p^3)	$[CuCl_5]^{3-}$
5	Square pyramid	dsp^3 (d_{x2-y2}, s, p^3)	$[Ni(CN)_5]^{3-}$
6	Octahedron	d^2sp^3 $(d_{x2-y2}, d_{z2}, s, p^3)$	$[Co(NH_3)_6]^{3+}$
6	Triangular prism	d^2sp^3 (d_{xz}, d_{yz}, s, p^3)	
6	Triangular prism	d^5s (d^5, s)	$[Mo(S_2C_2Ph_2)_3]$
7	Pentagonal bipyramid	d^3sp^3 $(d_{xy}, d_{x2-y2}, d_{z2}, s, p^3)$	$[V(CN)_7]^{4-}$
7	Capped triangular prism	d^3sp^3 $(d_{xy}, d_{xz}, d_{z2}, s, p^3)$	$[NbF_7]^{2-}$
8	Cube	sp^3d^3f $(s, p^3, d_{xy}, d_{xz}, d_{yz}, f_{xyz})$	$[Pa(CN)_8]^{4-}$
8	Dodecahedron	d^4sp^3 $(d_{z2}, d_{xy}, d_{xz}, d_{yz}, s, p^3)$	$[Mo(CN)_8]^{4-}$
8	Square antipirism	d^4sp^3 $(d_{x2-y2}, d_{xy}, d_{xz}, d_{yz}, s, p^3)$	$[TaF_8]^{3-}$
9	Tricapped triangular prism	d^5sp^3 (d^5, s, p^3)	$[ReH_9]^{2-}$

LINEAR COMPLEXES

$[Ag(NH_3)_2]^+$

$_{47}Ag : [Kr]\, 4d^{10} 5s^1$

$Ag^+ : [Kr]\, 4d^{10} 5s^0 5p^0$

$\quad\quad 4d \quad\quad 5s \quad 5p$

Ground state

Hibridization state

Complexation state

$$H_3N - Ag - NH_3 \quad (180°)$$

TETRAHEDRAL COMPLEXES

$[CoCl_4]^{2-}$

$_{27}Co : [Ar]\, 3d^7 4s^2$

$Co^{2+} : [Ar]\, 3d^7$

Ground state

Hibridization state

Complexation state

$Ni(CO)_4$

$[_{28}Ni] : \ldots 4s^2 3d^8$
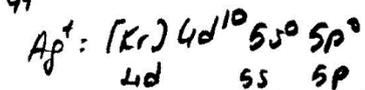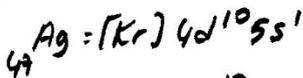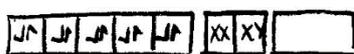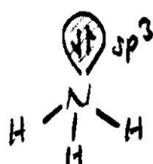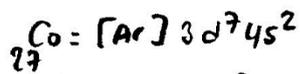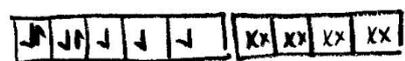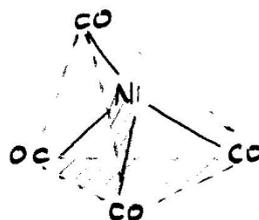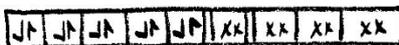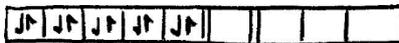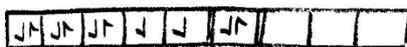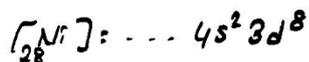
SQUARE PLANAR COMPLEXES

$[Ni(CN)_4]^{2-}$

$_{28}Ni: [Ar] 3d^8 4s^2$

$Ni^{2+}: [Ar] 3d^8 4s^0$

Ground state

Hibridization state

$dsp^2 \quad dsp^2 \quad dsp^2$

Complexation state
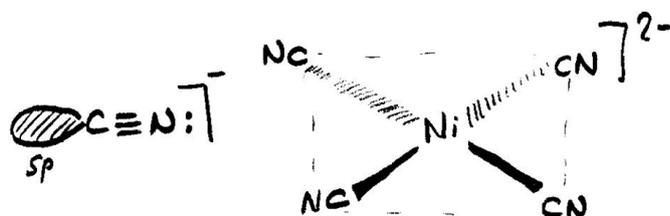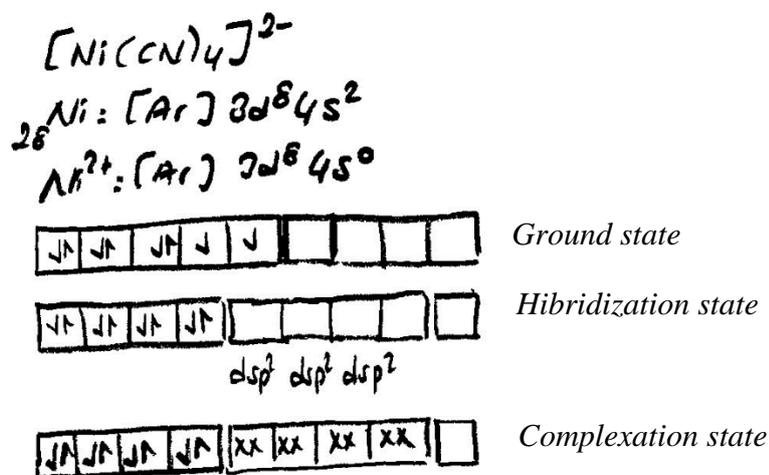
In $[Cu(NH_3)_4]^{2+}$ complex, tetrahedral and square planar structures are in equilibrium. However, tetrahedral structure was found in the solid state.

$[Cu(NH_3)_4]^{2+}$

$[_{29}Cu] = \cdots 4s^1 3d^{10}$

$Cu^{2+}: \quad 4s^0 3d^9$

dsp^2

sp^3
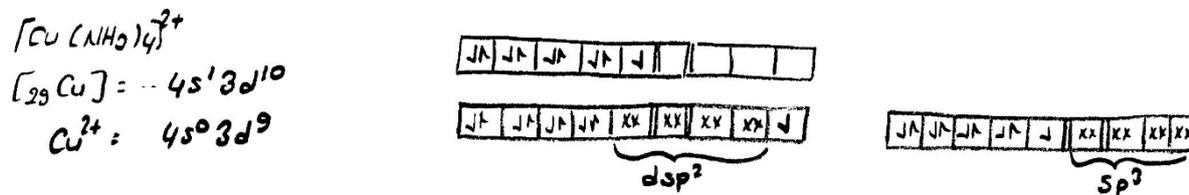
OCTAHEDRAL COMPLEXES

Valence bond theory divides octahedral complexes into two groups as inner orbital complexes and outer orbital complexes. Low-energy d orbital [(n-1) d] in the inner orbital complexes and high-energy d orbital (nd) in the outer orbital complexes participate in hybridization.

$[Fe(H_2O)_6]^{2+}$: sp^3d^2

$[Fe(CN)_6]^{3-}$: d^2sp^3

$[Cr(H_2O)_6]^{3+}$

$Cr^{3+}: [Ar]3d^3$
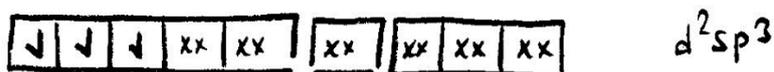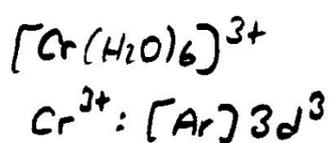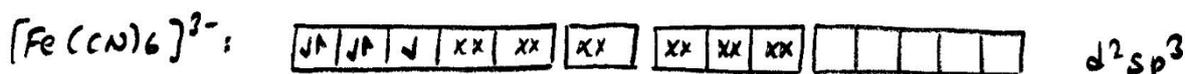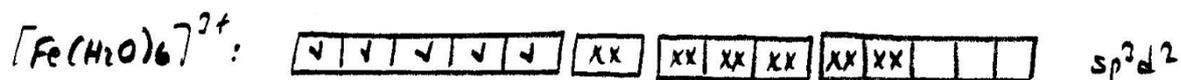
d^2sp^3

The empty d^2sp^3 hybrid orbitals of the Cr^{3+} ion overlaps with the full sp^3 hybrid orbital of H_2O ligand.

$[Ni(H_2O)_6]^{2+}$

$Ni^{2+} = [Ar]3d^8$

sp^3d^2
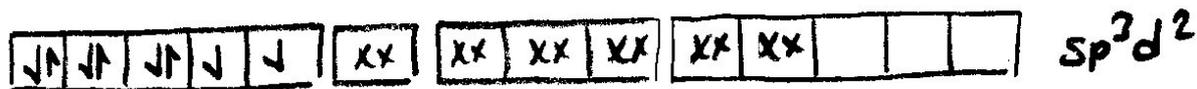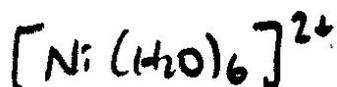
Central atom or ion in octahedral complexes

$d^{1-3} \rightarrow$ *only inner orbital complex*

$d^{7-10} \rightarrow$ *only outer orbital complex*

$d^{4-6} \rightarrow$ *both inner and external orbital complexes depending on the type of ligand*

The Co^{3+} ion can give both inner and external orbital complexes depending on the type of ligand. In the formation of $[Co(NH_3)_6]^{3+}$ complex ions, NH_3 ligands with more electron-donating properties can effectively match four single electrons of Co^{3+} ion, and the d^2sp^3 hybridization takes place using two empty 3d orbitals.
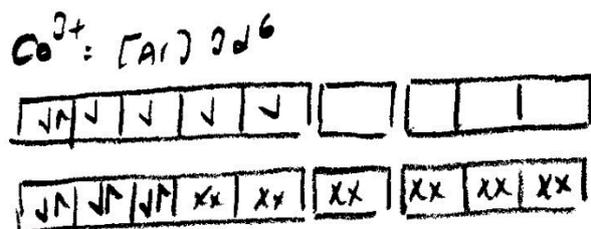
In the $[CoF_6]^{3-}$ ion, the electronegative F^- ligands cannot perform electron matching and form the paramagnetic outer orbital complex using 4d orbitals instead of 3d orbitals. According to the diagram, the compound has 4 unpaired electrons and exhibits paramagnetic behavior.
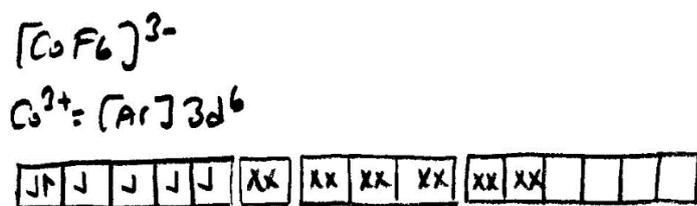
In the $[Co(NH_3)_6]^{2+}$ complex ion, the valence bond theory suggested that the electron in the half-full orbital passed the 5s orbital, and that the ligand electrons entered two 3d, one 4s and three 4p orbitals. In other words, $[Co(NH_3)_6]^{2+}$ is considered as the inner orbital complex. The electron, which is far from the nucleus, can easily leave the structure. This complex gives 1 e^- easily and transforms into the $[Co(NH_3)_6]^{3+}$ complex
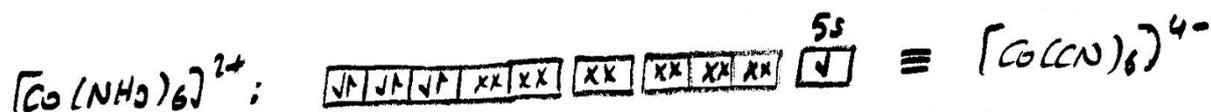
Result: Nitrogen donor ligands such as NH_3, NO_2^-, en, pyridine are strong ligands for cobalt.