

Lecture 6; CH 101: Inorganic Chemistry

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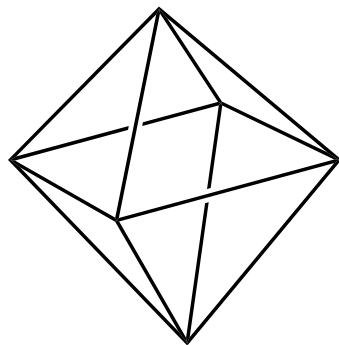
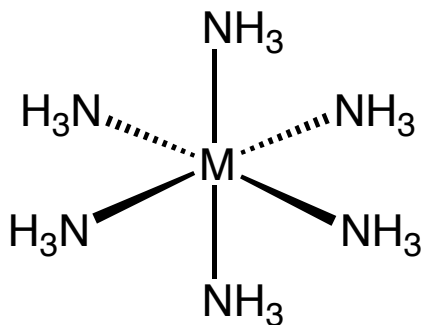
A Brief Review of Co-ordination Chemistry

✧ Co-ordination compound (complex)

An assembly of metal atom(s) and organic and/or inorganic groups (“Ligands”)

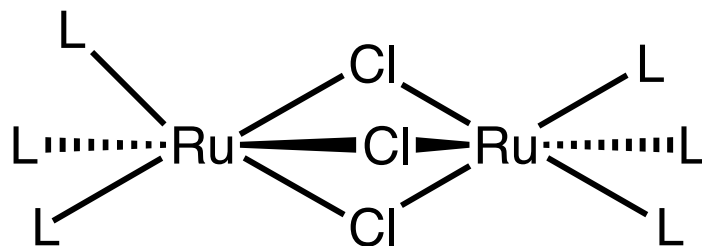
✧ Metal bound to non-carbon ligands –

Werner complexes

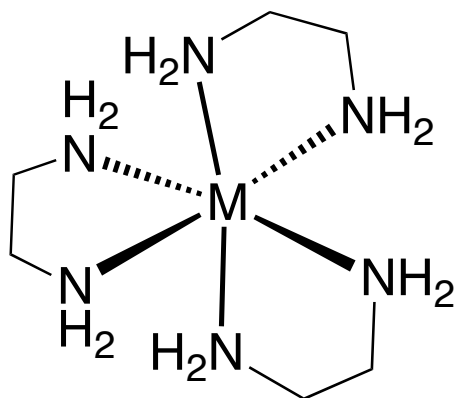


Lone pair on N donated to M
M is a polyvalent Lewis acid

- ✧ Ligands can have donor atoms having more than one lone pair



- ✧ There are also ligands which have more than one donor atoms



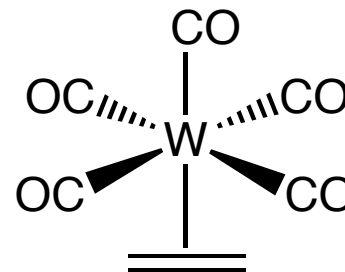
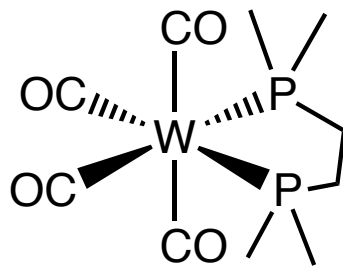
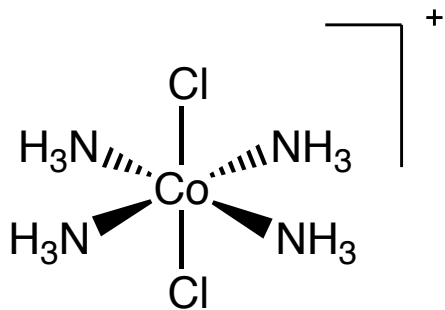
Very stable and less easily displaced compared to monodentate ligands

✧ Metal bound to organic ligands –
Organometallic complexes (M-C bond)

✧ Metal bound to organic ligands –
Metallo-organic complexes (M-XC bond, X= N, O)

✧ Co-ordination number

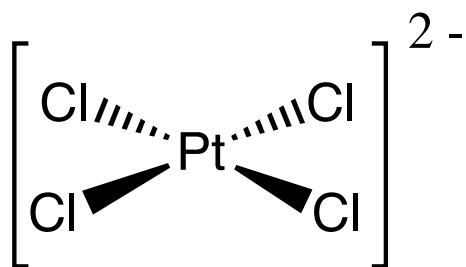
Number of groups bound to the central atom



✧ Oxidation state; $OS(M) = C_{\text{tot}} - L_{\text{tot}}$

C = Total charge of complex

L = Total charge of ligands

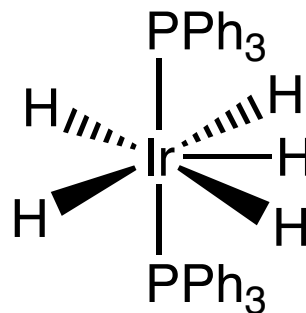


$$C = -2$$

$$L = 4 \times (-1) = -4$$

$$OS = -2 - (-4) = 2$$

How about $K_4[Fe(CN)_6]$ or



Actually oxidation state is only a formality

Bonding: Valence Bond Theory

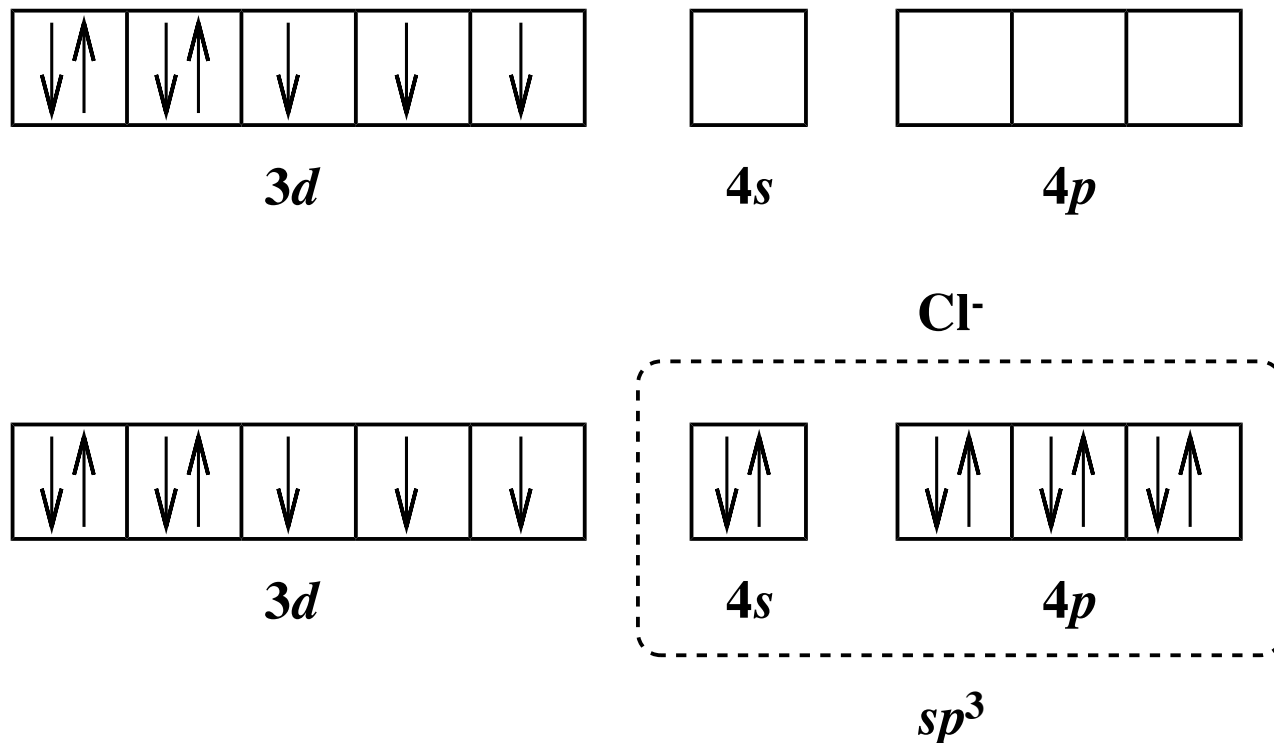
Overlapping of AOs of participating atoms

Filled orbital of ligand with empty orbital of metal

Geometry based on hybridization of metal ion

Bonding: Valence Bond Theory

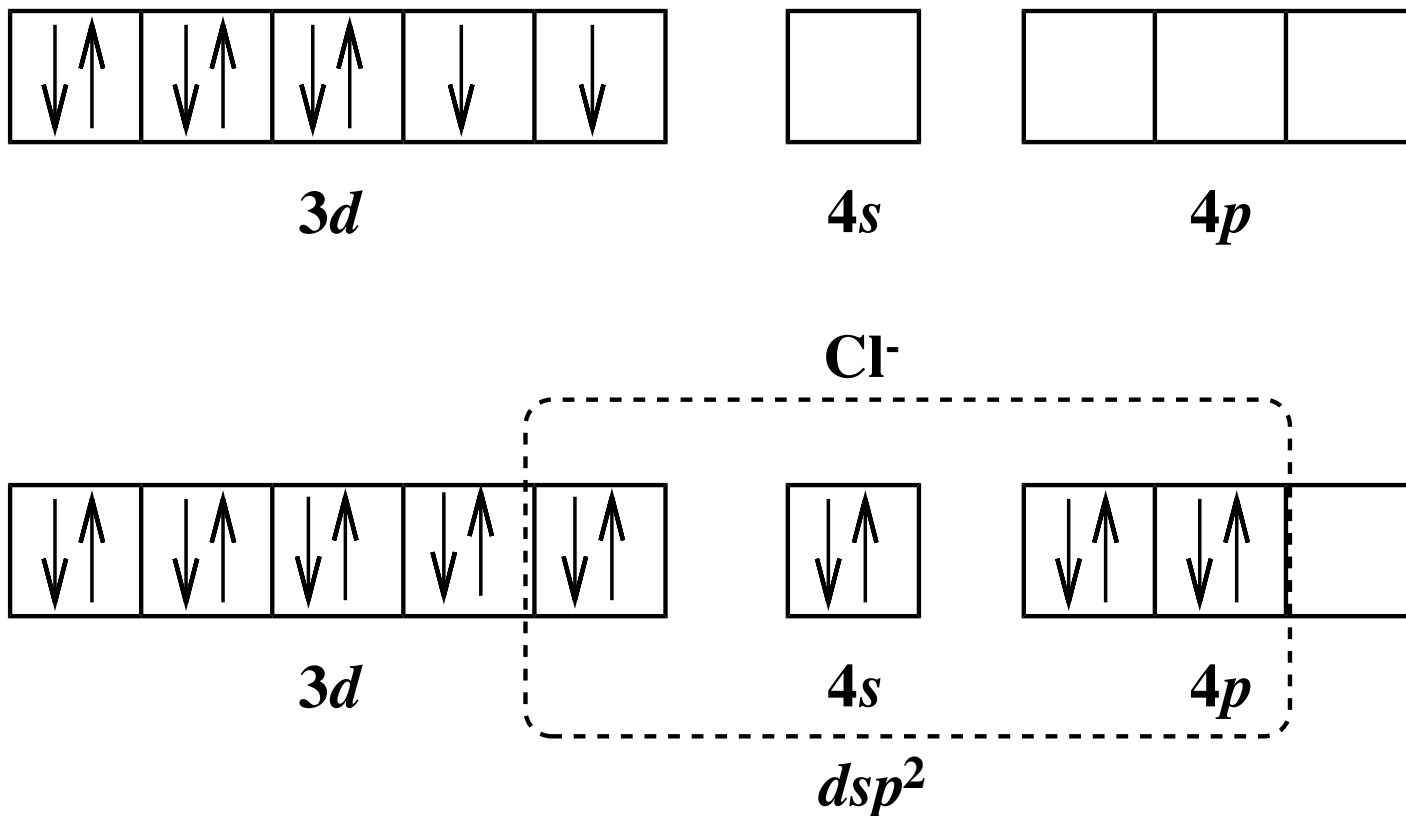
Geometry of $[\text{CoCl}_4]^{2-}$



4 co-ordinate, tetrahedral, paramagnetic

Bonding: Valence Bond Theory

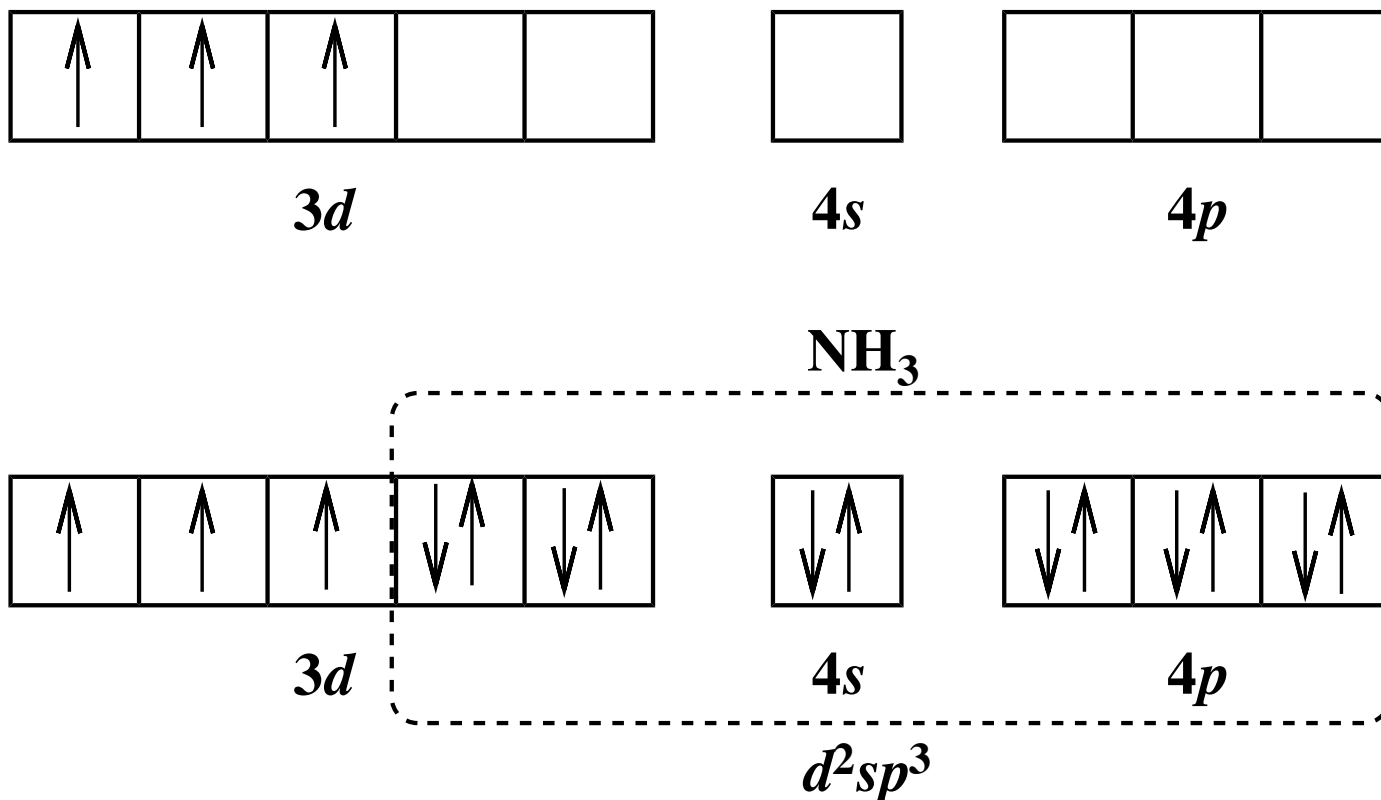
Geometry of $[\text{NiCN}_4]^{2-}$



4 co-ordinate, square planar, diamagnetic

Bonding: Valence Bond Theory

Geometry of $[\text{Cr}(\text{NH}_3)_6]^{3+}$



6 co-ordinate, octahedral, paramagnetic

Bonding: Valence Bond Theory

Geometry of $[\text{CoF}_6]^{3-}$ Vs. $[\text{Co}(\text{CN})_6]^{3-}$

Bonding Crystal Field Theory

Based on electrostatics

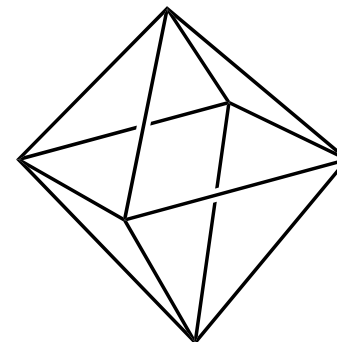
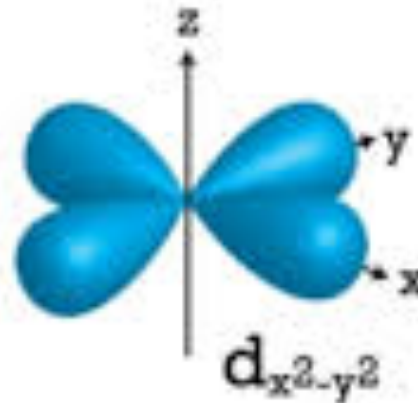
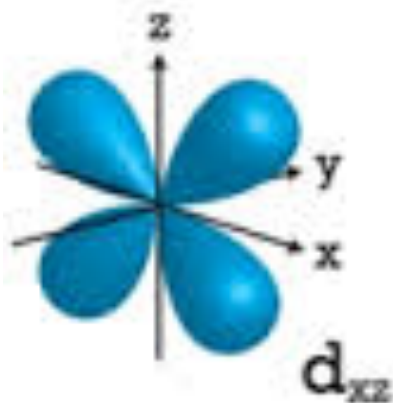
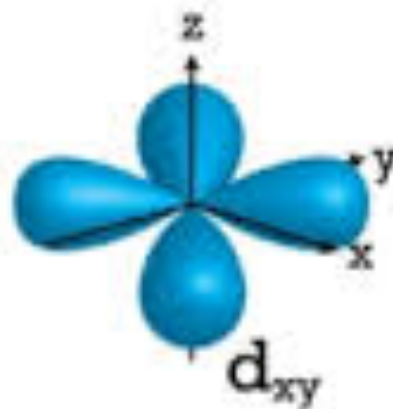
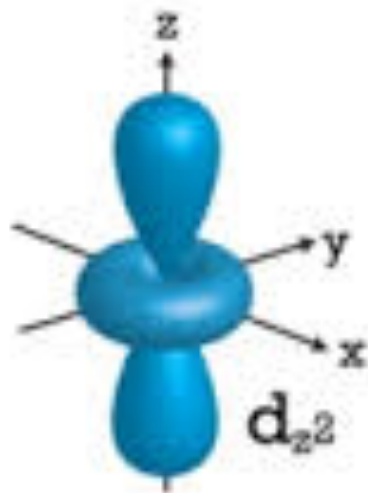
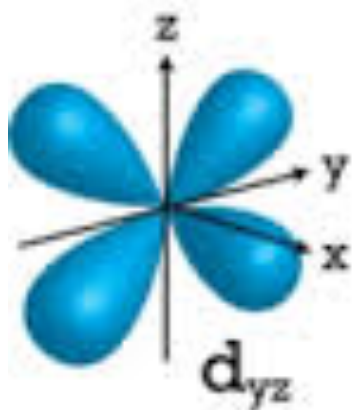
ligands are considered as point charges

All valence electrons are considered to be in d-orbitals

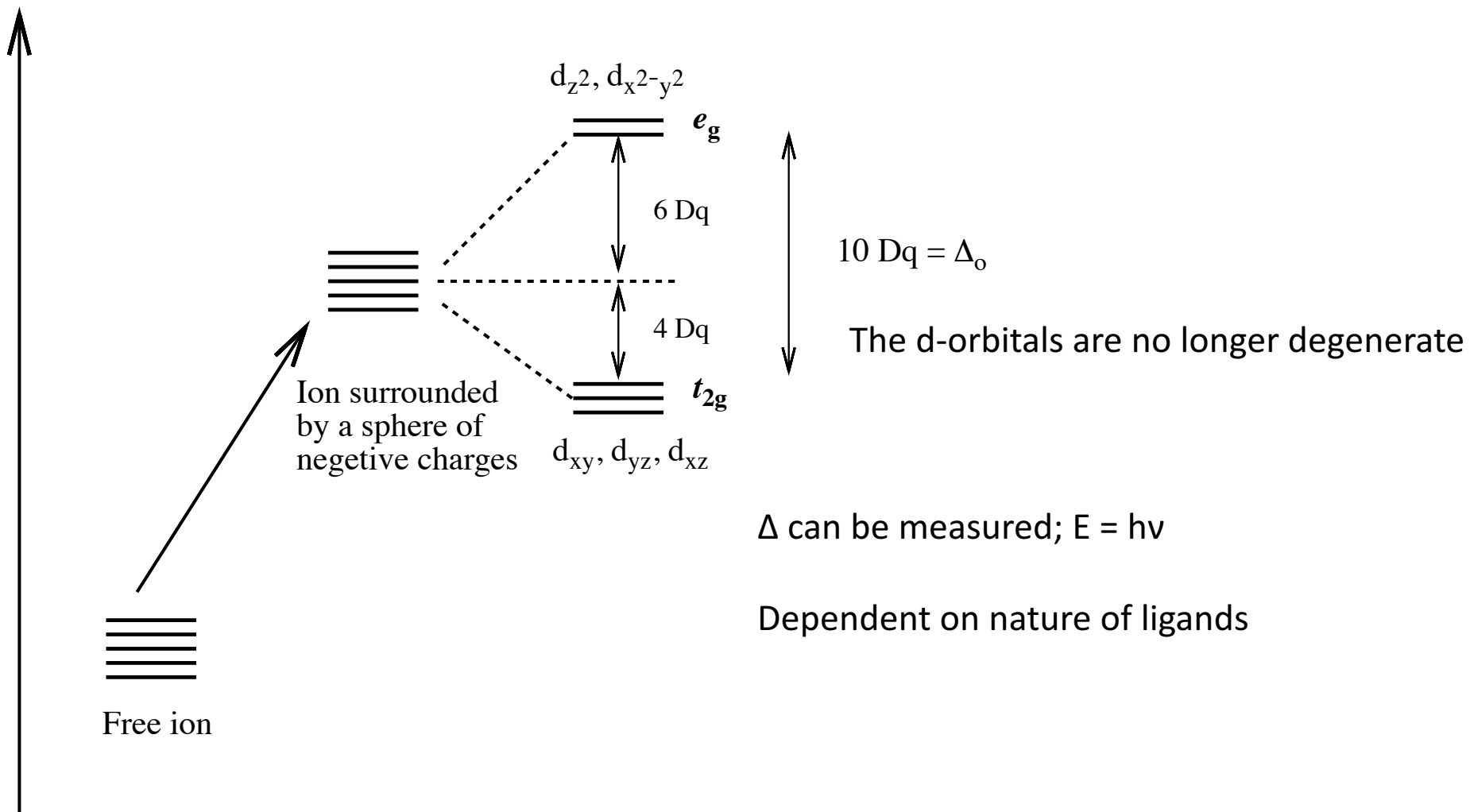
neutral free atom: $nd \sim (n+1)s$

complexes: $nd < (n+1)s < (n+1)p$

In neutral free atom, all d-orbitals have same energy (degenerate)



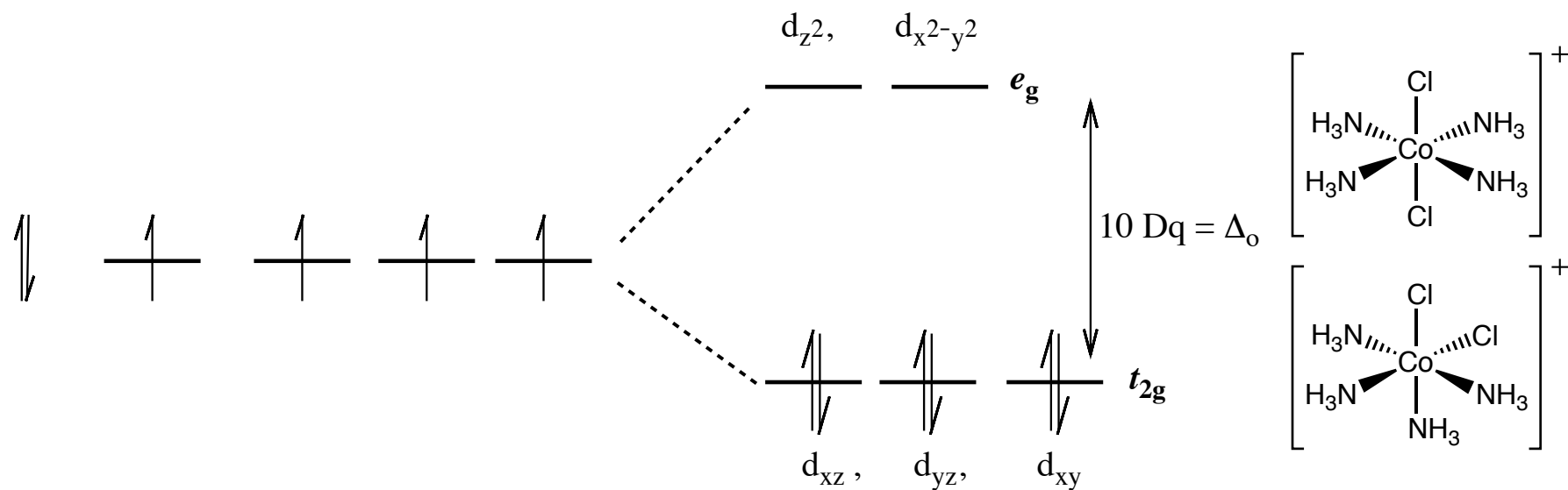
In an octahedral field



Co: $[\text{Ar}]4s^23d^7$

Co(0) complex: $[\text{Ar}]4s^03d^9$ (usually abbreviated as d^9)

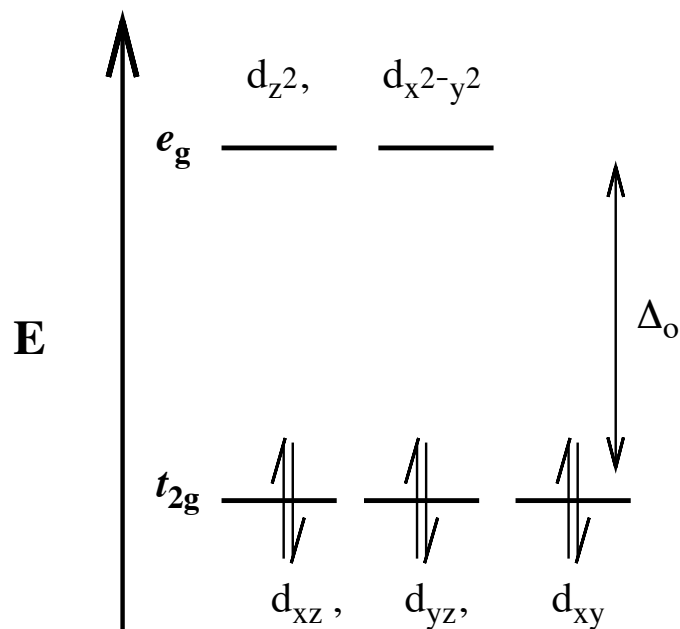
Co(III) complex: $[\text{Ar}]4s^03d^6$ (usually abbreviated as d^6)



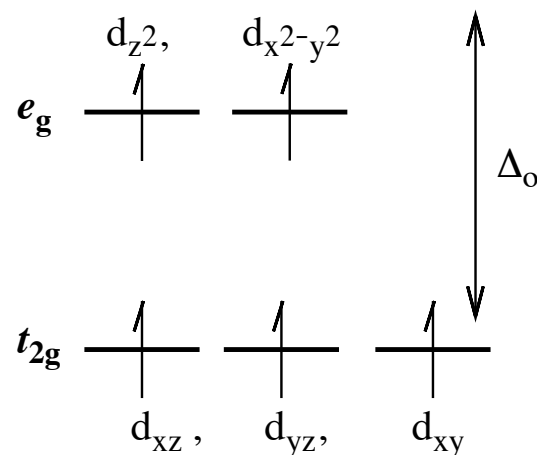
Co(II) d^7 – Labile; Co(III) d^6 – inert; Cr(III) d^3 – inert
2nd and 3rd row complexes mostly inert – high Δ

d^6 configuration is very stable and commonest type

Other examples include Mo(0), Re(I), Fe(II) & Pt(IV)



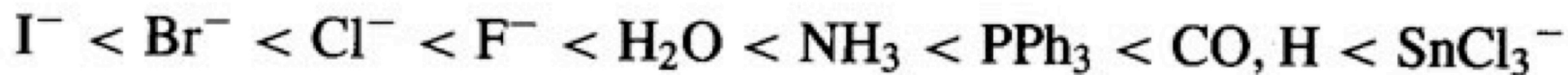
Pairing energy $< \Delta_o$
Low-spin complexes
Diamagnetic



Pairing energy $> \Delta_o$
High-spin complexes
Paramagnetic

- ✧ Complexes with odd number of electrons;
 $d^5 \text{V(CO)}_6$ – paramagnetic
- ✧ Complexes with even number of electrons
High-spin for first row transition elements
- ✧ *High-field* ligands (CO , C_2H_4): low-spin complexes
- ✧ Low-field ligands (H_2O , NH_3): High-spin complexes

Spectrochemical Series



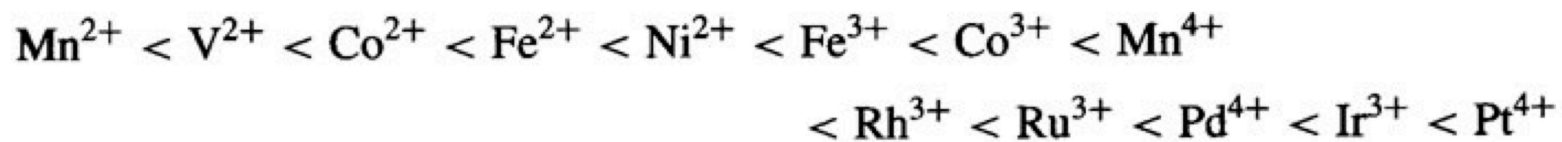
← low Δ

high Δ →

← π donor

π acceptor/strong σ donor →

- (i) Δ_o increases with increase in ligand field strength.
- (ii) For a given ligand, Δ_o increases with increase in oxidation state of the metal ion.
- (iii) For a given ligand and a given oxidation state, Δ_o increases down a group (3d < 4d < 5d).



← low Δ

high Δ →

← low valent, first row

high valent, third row →