Strong field Vs. Weak Field ligands

Strong field ligands	Weak field ligands
These are the ligands used in octahedral complexes in which the crystal field stabilization energy Δ_0 is greater than pairing energy (p).	These are the ligands used in octahedral complexes in which the crystal field stabilization energy Δ_0 is less than pairing energy (p) in a single orbital.
Contains C, N and P as donor sites.	Contains X, O and S as donor atoms
Complexes formed by these ligands are also known as low spin complexes.	Complexes formed by these ligands are also known as high spin complexes.
The complexes formed are mostly diamagnetic or comparatively less paramagnetic in nature.	The complexes formed are generally paramagnetic in nature.

Spectrochemical series

- In 1938, the Spectrochemical series was established, which is a list of ligands organized by strength or a list of metal ions organized by oxidation number, group, and identity.

- Weak field ligands and strong field ligands are the two types of ligands.

- Strong field ligands, on the other hand, are those that cause a big crystal field splitting and so have a low spin value, whereas weak field ligands have a low crystal field splitting and hence have a high value.

- A series that arrange the ligands from large splitting value to small splitting value is known as spectrochemical

$$I^- < Br^- < SCN^- < Cl^- < S^{-2} < N_3^- < F^- < ONO^- < OH^- < SO_4^{-2} < NO_4^-$$

$$< C_2O_4^{-2} < O^{-2} < H_2O \sim NCS^- < EDTA^{-4} < NH_3 \sim Py < en < bpy \sim phen$$

$$< NO_2^- < PR_3 < CH_3 < CN^- \sim CO$$

From I^- To H_2O are weak field ligands

From NCS^- To CO are strong field ligands

Pairing Energy (P)

The pairing energy is not an experimentally obtained value like Δ_o and is same for a metal ion irrespective of the ligands. It is made up of two terms.

1) The inherent coulombic repulsion that must be overcome when two electrons are forced to occupy the same orbital. *(Destabilizing energy contribution of P_c for each doubly occupied orbital).*

2) Loss of exchange energy (based on Hunds rule) that occurs as two electrons with parallel spin (↑↑) are forced to become antiparrallel (↑↓) in an orbital. *(contribution of P_e for each pair having same spin and same energy)*

P = sum of all P_c and P_e interactions
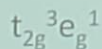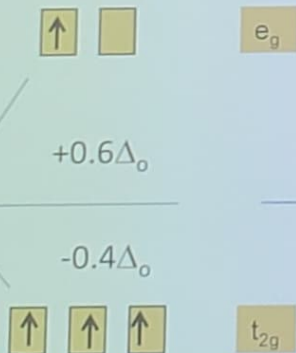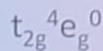
Crystal Field Stabilization Energy (CFSE)

- The Crystal Field Stabilization Energy is defined as the energy of the electron configuration in the ligand field minus the energy of the electronic configuration in the isotropic field.

$$CFSE = \Delta E = E_{\text{ligand field}} - E_{\text{isotropic field}}$$

The CSFE will depend on multiple factors including:

1. Geometry (which changes the d-orbital splitting patterns)
2. Number of d-electrons
3. Spin Pairing Energy
4. Ligand field strength (via Spectrochemical Series)

For an octahedral complex, an electron in the more stable t_{2g} subset is treated as contributing $-2/5\Delta o$ whereas an electron in the higher energy e_g subset contributes to a destabilization of $+3/5\Delta o$. The final answer is then expressed as a multiple of the crystal field splitting parameter Δo. If any electrons are paired within a single orbital, then the term P is used to represent the spin pairing energy.
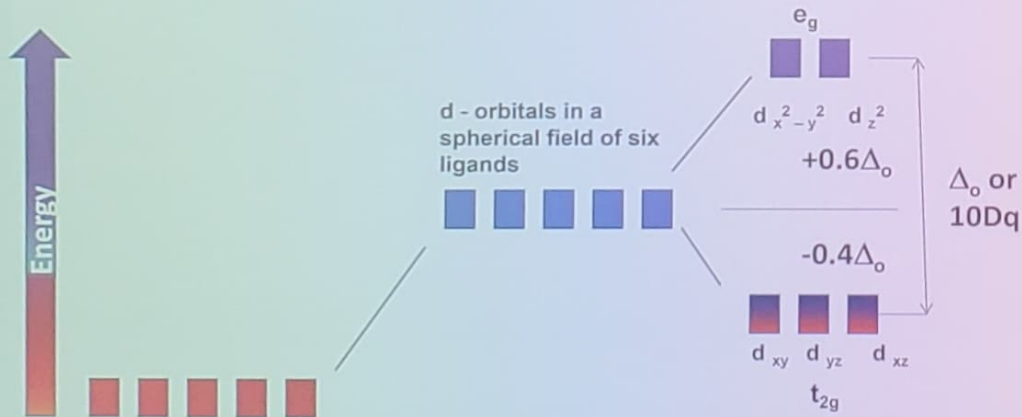
- In octahedral field, configuration is: $t_{2g}^{x} e_{g}^{y}$
- Net energy of the configuration relative to the average energy of the orbitals is: $= (-0.4x + 0.6y)\Delta_O$
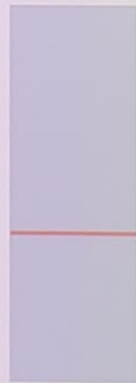
$$\Delta_O = 10 \ Dq$$

Beyond d^3

- In weak field: $\Delta_O < P, \ => \ t_{2g}^{3} e_{g}^{1}$
- In strong field $\Delta_O > P, \ => \ t_{2g}^{4}$

Splitting of the d-orbitals in an octahedral field

Spherical environment

In octahedral crystal field

e_g

d - orbitals in a spherical field of six ligands

$d_{x^2-y^2}$ d_{z^2}

$+0.6\Delta_o$

Δ_o or 10Dq

$-0.4\Delta_o$

d_{xy} d_{yz} d_{xz}

t_{2g}

e_g

$\frac{3}{5}\Delta_O$

Δ_O

$\frac{2}{5}\Delta_O$

t_{2g}

Energy

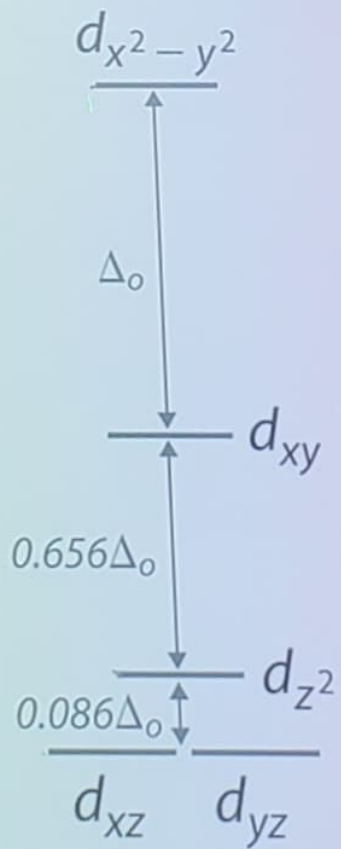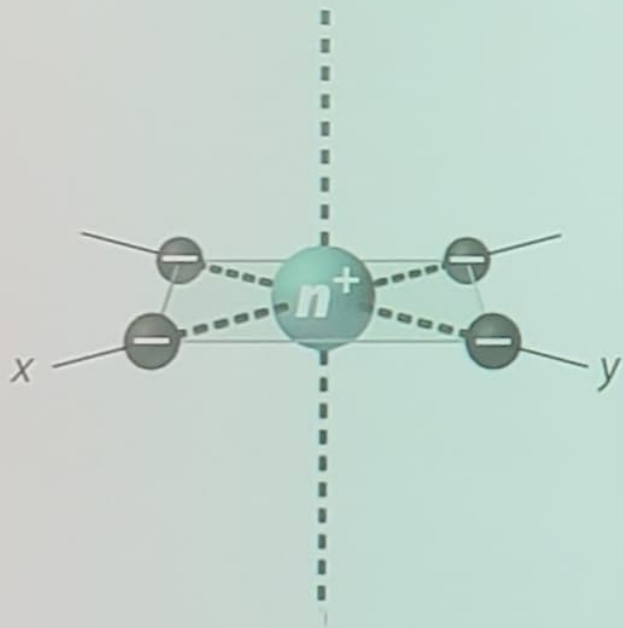d - orbitals stabilized by metal-ligand electrostatic attraction

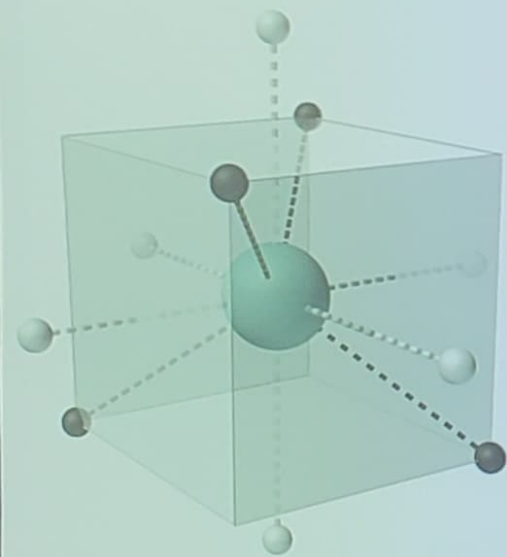t_{2g} : triply degenerate set of orbitals :
e_g doubly degenerate set of orbitals
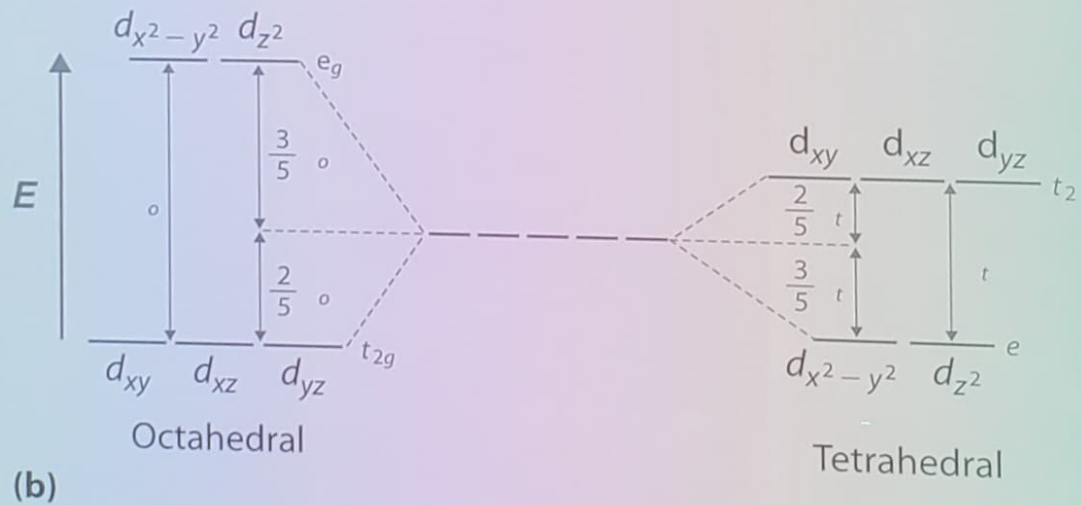g= gerade: symmetric with respect to the centre of inversion
u= ungerade : antisymmetric w. r. t the centre of inversion

Barycenter: A point between objects where they balance each other
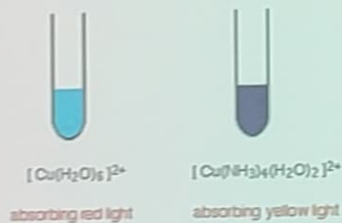
(a)

(b)

Octahedral

Tetrahedral

Spectrochemical series

$$I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < Ox < ONO^- < H_2O \quad \text{Weak field}$$

$$< NCS^- < edta^{4-} < NH_3 \sim Py < en < bipy < Phen < NO_2^- < PPh_3 < CN^- \sim CO \quad \text{Strong field}$$

Halides ; sulfur donors < Oxygen donors < Nitrogen donors < CN-, CO

e_g

$0.6\ \Delta_0$

$0.4\ \Delta_0$

t_{2g}

Spherical field   Weak field   Strong field

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

absorbing red light

$[Cu(NH_3)_4(H_2O)_2]^{2+}$

absorbing yellow light

COBALT(III) Complexes of
(a) CN⁻, (b) NO₂⁻, (c) phen, (d) en, (e) NH₃, (f) gly, (g) H₂O, (h) ox²⁻, (i) CO₃²⁻
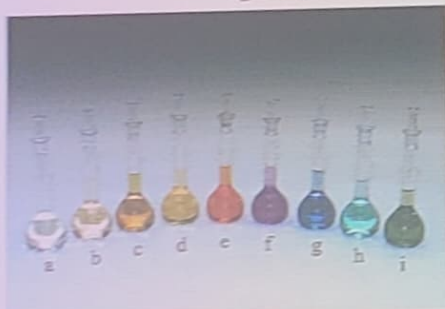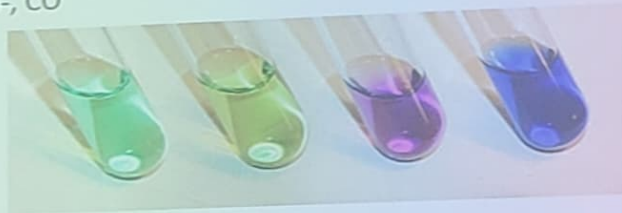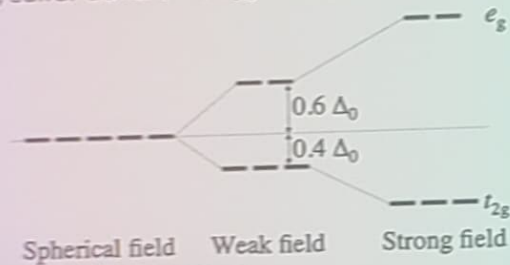
Stepwise addition of 'en' to $[Ni(H_2O)_6]^{2+}$

High Spin Vs. Low Spin (d^1 to d^{10})

- How complexes prefer to adopt High Spin/ low spin arrangement of electrons?

Ans: Δ_o < Pairing energy : High Spin $\qquad$ Δ_o > Pairing Energy : Low Spin
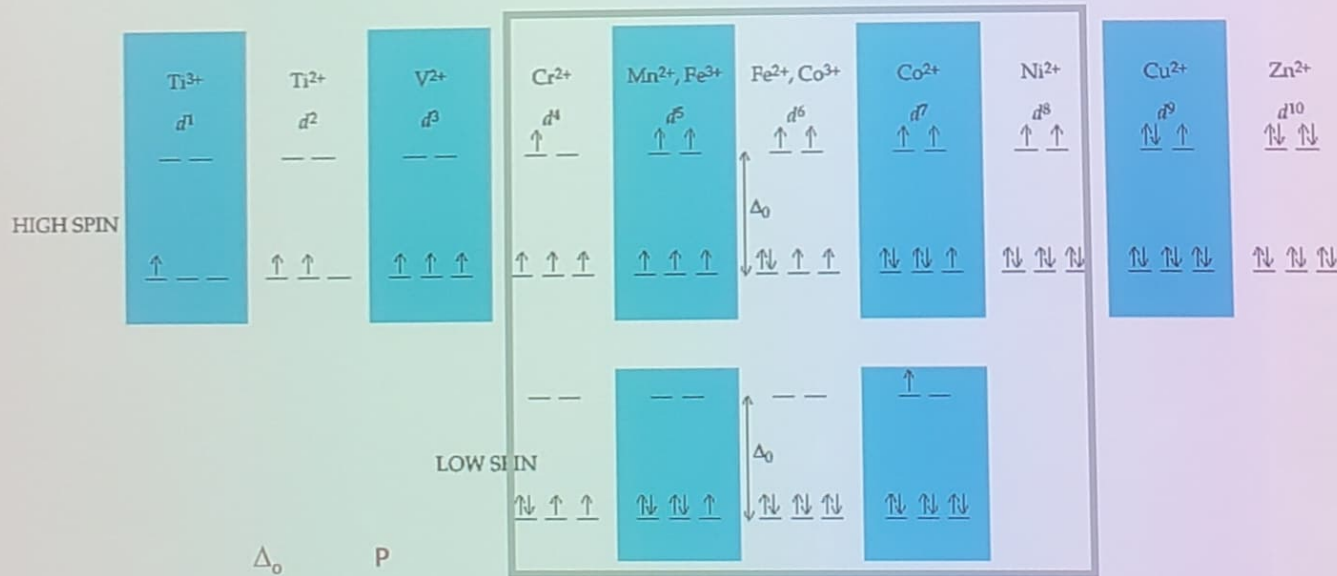
Complex	Δ_o	P		
$[Fe(H_2O)_6]^{2+}$ d^6	9350	19150	High Spin	$\Delta_o < P$
$[Fe(CN)_6]^{4-}$ d^6	32200	19150	Low Spin	$\Delta_o > P$

HIGH SPIN

LOW SPIN

Ti³⁺ d^1, Ti²⁺ d^2, V²⁺ d^3, Cr²⁺ d^4, Mn²⁺, Fe³⁺ d^5, Fe²⁺, Co³⁺ d^6, Co²⁺ d^7, Ni²⁺ d^8, Cu²⁺ d^9, Zn²⁺ d^{10}

Total d-electrons	Octahedral configuration	CFSE	Tetrahedral configuration	CFSE	OSPE
d^0	t_{2g}^0	$0\,\Delta o$	e^0	$0\,\Delta t$	$0\,\Delta o$
d^1	t_{2g}^1	$-2/5\,\Delta o$	e^1	$-3/5\,\Delta t$	$-6/45\,\Delta o$
d^2	t_{2g}^2	$-4/5\,\Delta o$	e^2	$-6/5\,\Delta t$	$-12/45\,\Delta o$
d^3	t_{2g}^3	$-6/5\,\Delta o$	$e^2 t_2^1$	$-4/5\,\Delta t$	$-38/45\,\Delta o$
d^4	$t_{2g}^3 e_g^1$	$-3/5\,\Delta o$	$e^2 t_2^2$	$-2/5\,\Delta t$	$-19/45\,\Delta o$
d^5	$t_{2g}^3 e_g^2$	$0\,\Delta o$	$e^2 t_2^3$	$0\,\Delta t$	$0\,\Delta o$
d^6	$t_{2g}^4 e_g^2$	$-2/5\,\Delta o + P$	$e^3 t_2^3$	$-3/5\,\Delta t + P$	$-6/45\,\Delta o$
d^7	$t_{2g}^5 e_g^2$	$-4/5\,\Delta o + 2P$	$e^4 t_2^3$	$-6/5\,\Delta t + 2P$	$-12/45\,\Delta o$
d^8	$t_{2g}^6 e_g^2$	$-6/5\,\Delta o + 3P$	$e^4 t_2^4$	$-4/5\,\Delta t + 3P$	$-38/45\,\Delta o$
d^9	$t_{2g}^6 e_g^3$	$-3/5\,\Delta o + 4P$	$e^4 t_2^5$	$-2/5\,\Delta t + 4P$	$-19/45\,\Delta o$
d^{10}	$t_{2g}^6 e_g^4$	$0\,\Delta o$	$e^4 t_2^6$	$0\,\Delta t$	$0\,\Delta o$

Tetrahedral Splitting

d_{xy} d_{yz} d_{zx}

$+0.4\,\Delta t$

$-0.6\,\Delta t$

$d_{x^2-y^2}$ d_{x^2}

d^6

$d_{x^2-y^2}$ d_{x^2}
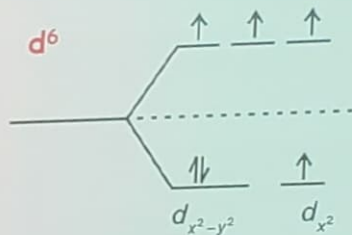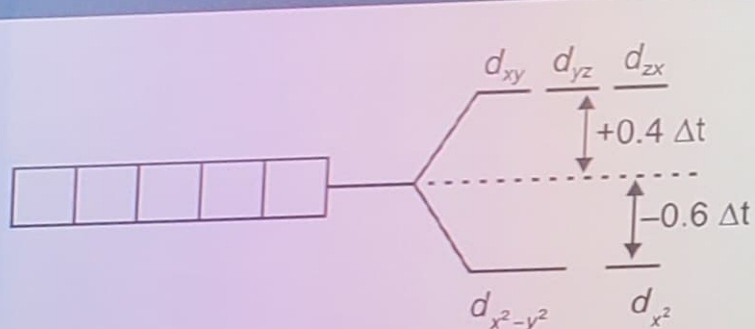
(Tetrahedral complexes are always high spin complexes)

$-3(0.6)+3(0.4)=-0.6\,\Delta_t$

Octahedral vs. Tetrahedral

$ML_6\ (O_h)$

$d_{x2-y2}\ d_{z2}$

e_g

Δ_o

t_{2g}

$d_{xy}\ d_{yz}\ d_{xz}$

$ML_4\ (T_d)$

$d_{xy}\ d_{yz}\ d_{xz}$

t_2

Δ_t

e

$d_{x2-y2}\ d_{z2}$

Not t_{2g}
and
e_g
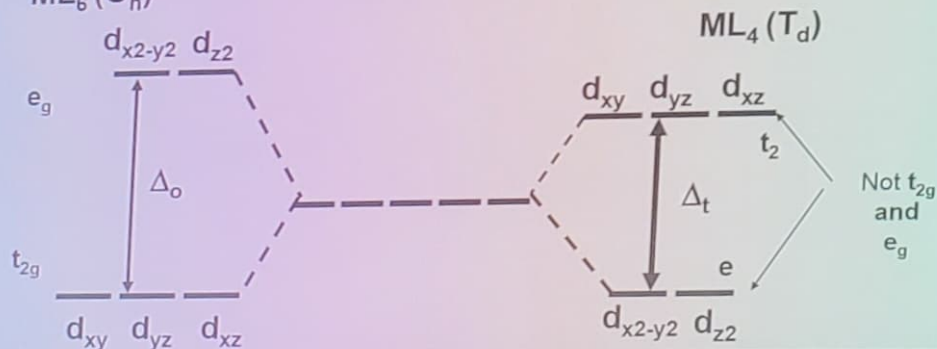
T_d Vs O_h Splitting

- The Crystal Field Stabilization Energy (CFSE) is the additional stabilization gained by the splitting of the orbitals according to the **CFT** against the energy of the original five degenerate d orbitals.

Example: in a d^1 situation such as $[Ti(OH_2)_6]^{3+}$, putting the electron into one of the orbitals of the t_{2g} level gains $-0.4\,\Delta_o$ of CFSE. The O ctahedral complexes will be favored over tetrahedral ones because
> 1. It is more (energetically) favorable to form six bonds rather than four
> 2. The CFSE is usually greater for octahedral than tetrahedral complexes (Δo is bigger than Δ_{tet} (in fact, Δ_{tet} is approximately $4/9\,\Delta_o$).

- If we assumes, $\Delta_{tet} = 4/9\,\Delta_o$, we can calculate the difference in stabilization energy between octahedral and tetrahedral geometries by referencing everything in terms of Δo.

- Which is the preferred configuration for a d^3 metal: tetrahedral or octahedral?

    To answer this, the Crystal Field Stabilization Energy has to be calculated for a (d^3 metal in both configurations. The geometry with the greater stabilization will be the preferred geometry)

T_d Vs O_h Splitting

- d^3 O_h configuration, the Crystal Field Stabilization Energy is

$$CFSE = 3 \times -0.4\Delta_o = -1.2 \, \Delta_o$$

- d^3 Td configuration

$$CFSE = 0.8\Delta_{tet}$$

- Because Δ_{tet} is less than half the size of Δ_o, tetrahedral complexes are often high spin. We can now put this in terms of Δ_o (we can make this comparison because we're considering the same metal ion and the same ligand: all that's changing is the geometry)

   So for tetrahedral d_3, the Crystal Field Stabilization Energy is:
$$CFSE = -0.8 \times 4/9 \, \Delta_o = -0.355 \, \Delta_o.$$

- The difference in Crystal Field Stabilization Energy between the two geometries will be:

$$1.2 - 0.355 = 0.845 \, \Delta_o.$$

T_d Vs O_h Splitting

This table compares the values of the CFSE for octahedral and tetrahedral geometries, assuming high spin configurations. The units are Δ_o, and we're assuming that $\Delta_{tet} = 4/9\ \Delta_o$.

	O_h	T_d	Difference
d^0, d^5, d^{10}	0	0	0
d^1, d^6	0.4	0.27	0.13
d^2, d^7	0.8	0.53	0.27
d^3, d^8	1.2	0.36	0.84
d^4, d^9	0.6	0.18	0.42

The ordering of favorability of octahedral over tetrahedral is: $d^3, d^8 > d^4, d^9 > d^2, d^7 > d^1, d^6 > d^0, d^5, d^{10}$