TRANSITION METALS
CRYSTAL FIELD THEORY (CFT)

DR. MIOY T. HUYNH | 2020
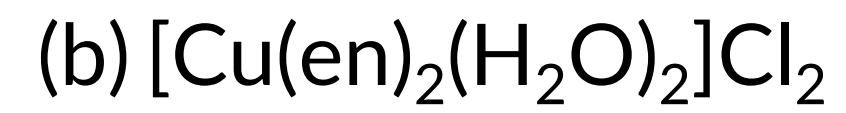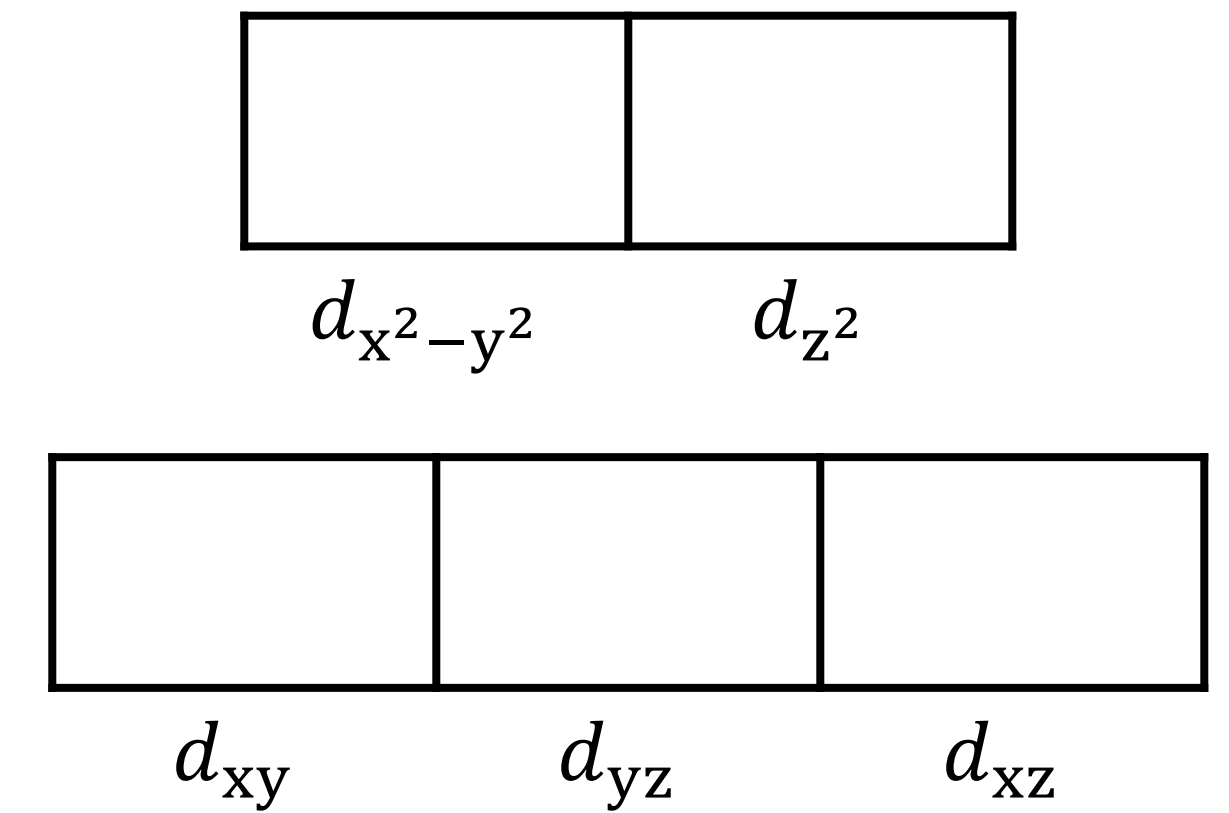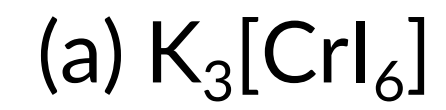
CHEMISTRY 165 // SPRING 2020

PRACTICE PROBLEM 1

Predict the number of unpaired electrons in the following coordination compounds.

— answer —
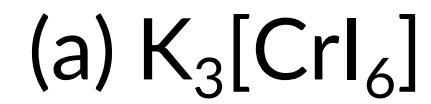
(a) $K_3[CrI_6]$

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

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

(b) $[Cu(en)_2(H_2O)_2]Cl_2$

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

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

PRACTICE PROBLEM 1

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— answer —

(a) $K_3[CrI_6]$

First, determine the oxidation state of the metal center: Cr(III).
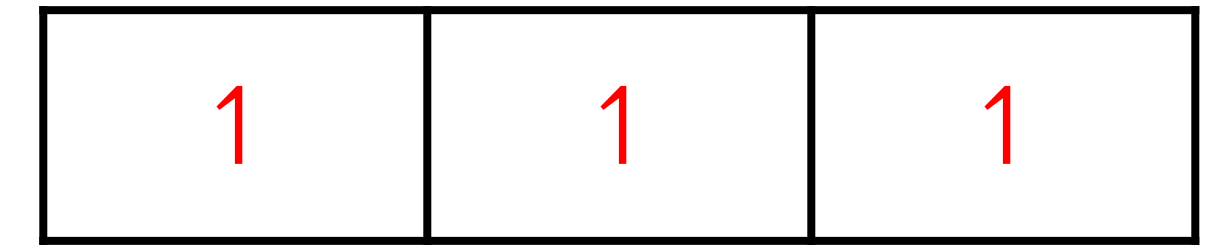
Neutral Cr atom has an electronic configuration of $[Ar]4s^1 3d^5$; therefore, Cr^{3+} has an electronic configuration of $[Ar]3d^3$. Now we can fill the <u>three</u> d-electrons into the crystal field diagram to find there are <u>three unpaired electrons</u>.

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

1	1	1

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

(b) $[Cu(en)_2(H_2O)_2]Cl_2$

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

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

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— answer —

(a) $K_3[CrI_6]$

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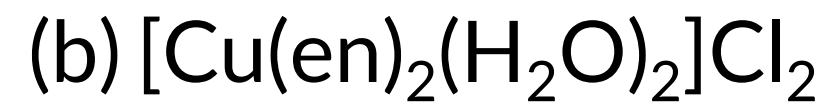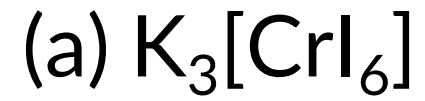
$d_{x^2-y^2}$	d_{z^2}

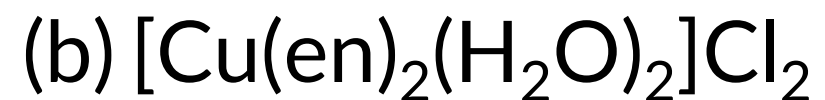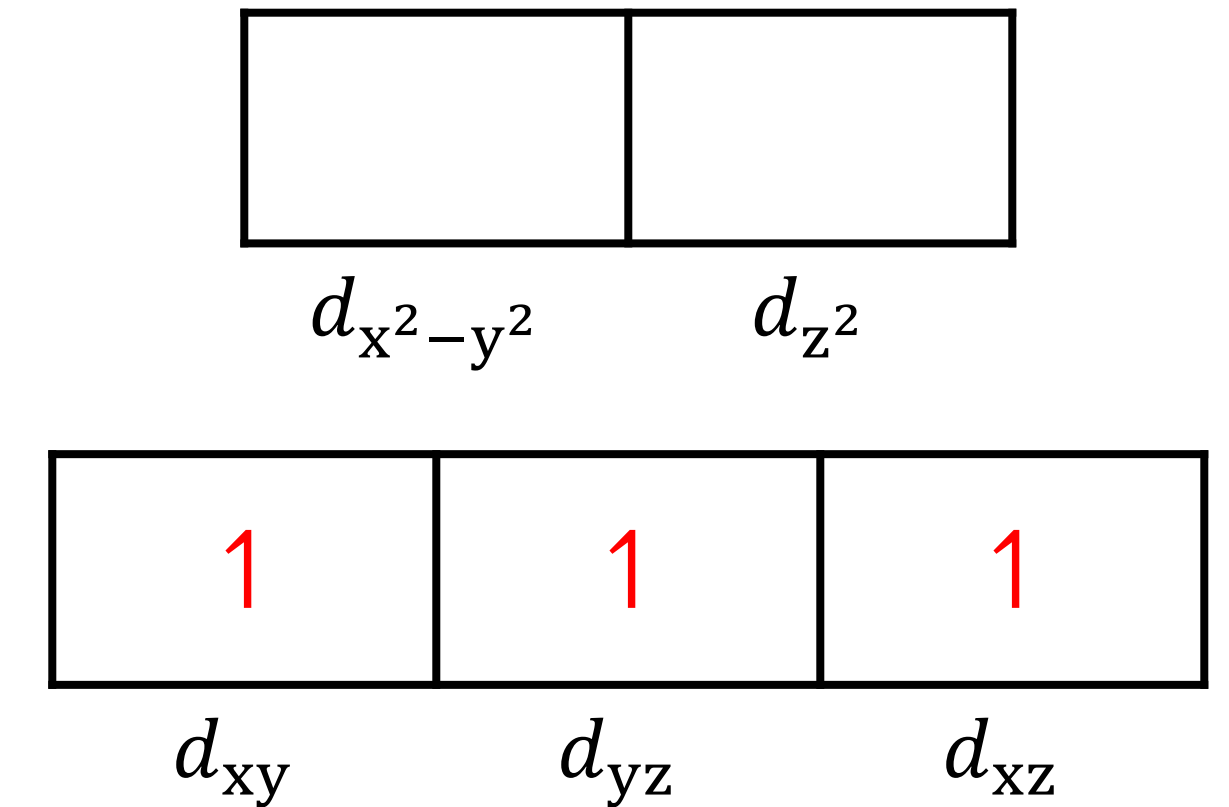| 1	1	1
d_{xy}	d_{yz}	d_{xz}

(b) $[Cu(en)_2(H_2O)_2]Cl_2$

First, determine the oxidation state of the metal center: Cu(II).

Neutral Cu atom has an electronic configuration of $[Ar]4s^13d^{10}$; therefore, Cu^{2+} has an electronic configuration of $[Ar]3d^9$. Now we can fill the <u>nine</u> d-electrons into the crystal field diagram to find there is <u>one unpaired electrons</u>.

1↓	1
$d_{x^2-y^2}$	d_{z^2}

1↓	1↓	1↓
d_{xy}	d_{yz}	d_{xz}

PRACTICE PROBLEM 2

Predict the number of unpaired electrons in the complex ion: $[Co(NO_2)_6]^{3-}$.

Spectrochemical series: $CN^- > NO_2^- > CN^- > en > NH_3 > H_2O > F^- > Cl^- > Br^- > I^-$

— answer —

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

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

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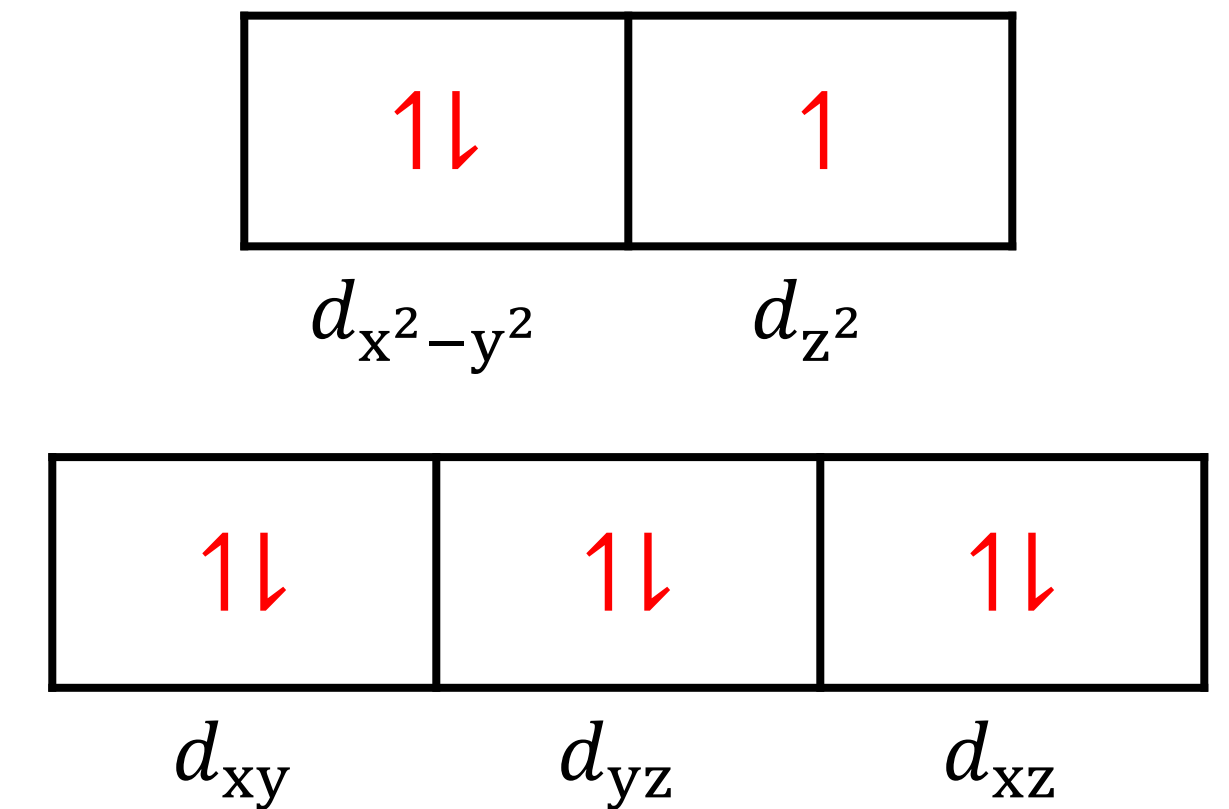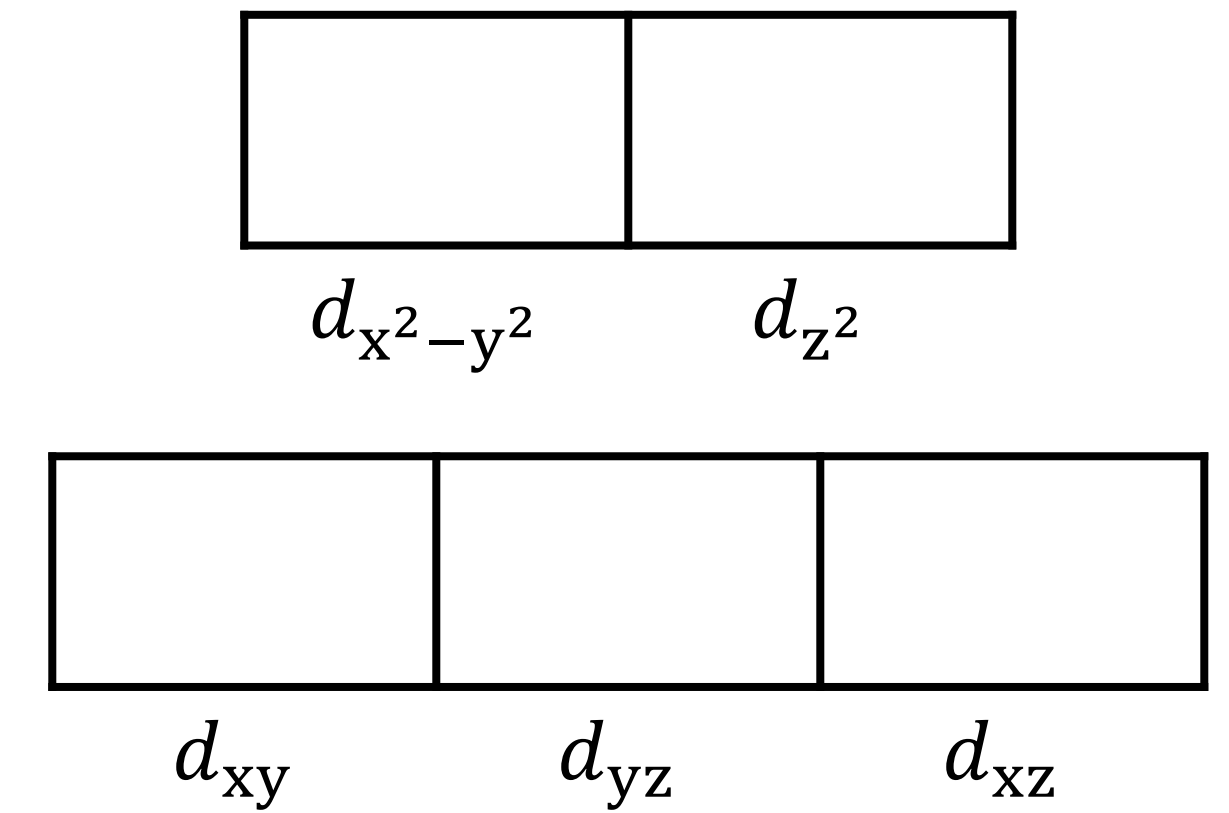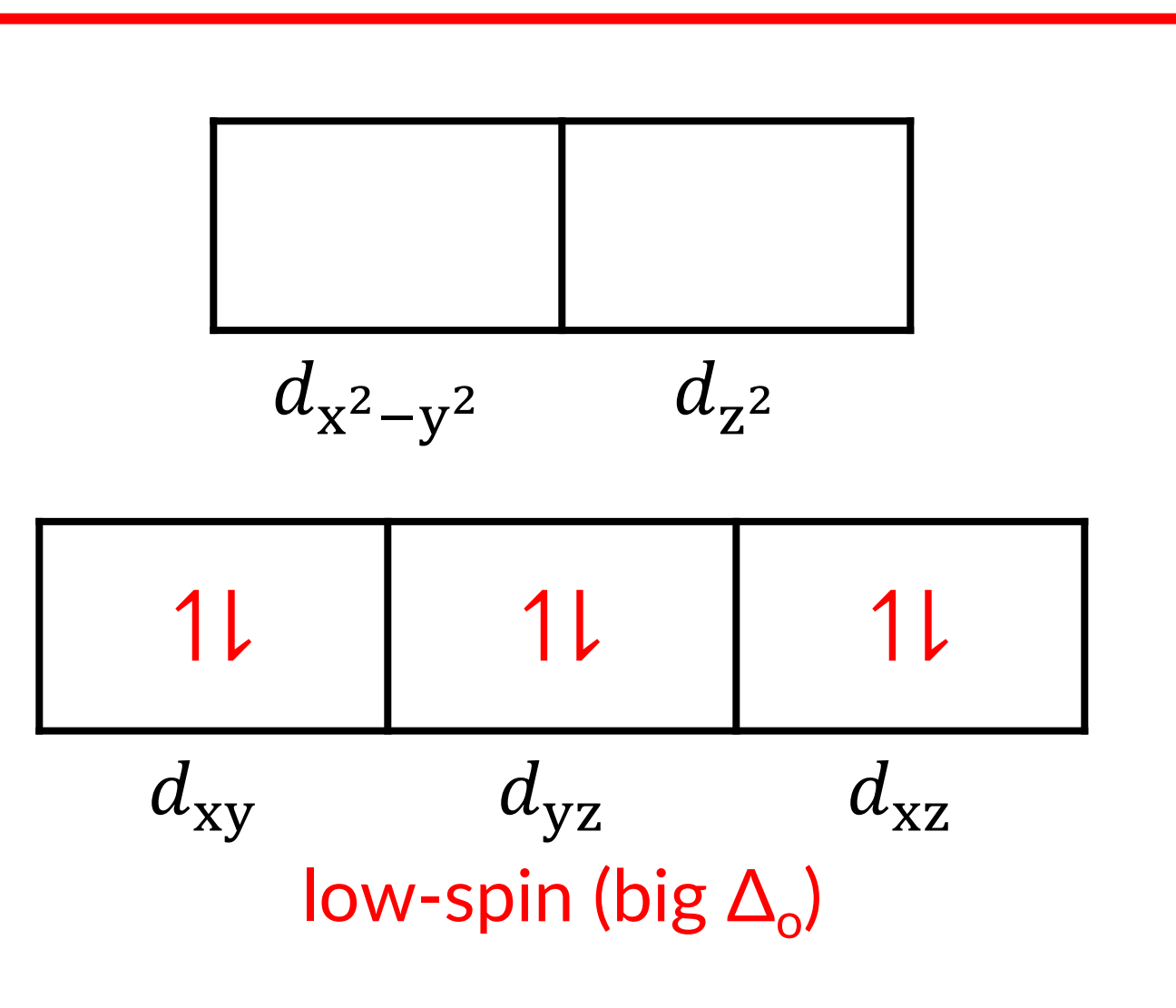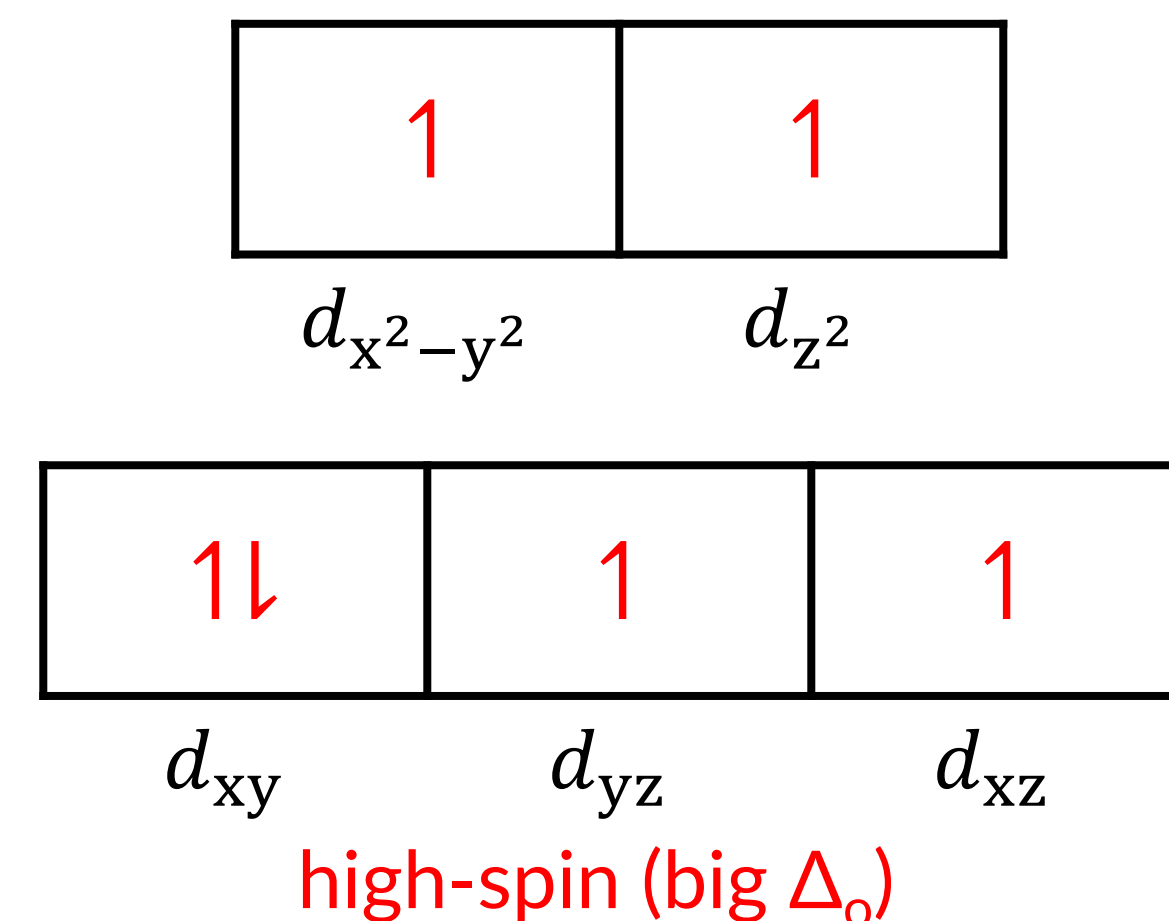
First, determine the oxidation state of the metal center: Co(III).

Neutral Co atom has an electronic configuration of $[Ar]4s^2 3d^7$; therefore, Co^{2+} has an electronic configuration of $[Ar]3d^6$. This is a spin-ambiguous case because we can either have a high-spin or a low-spin configuration.

However, the ligand is NO_2^-, which is a <u>strong-field</u> ligand that <u>increases</u> the splitting between the two sets of d-orbitals (the energy difference is denoted Δ_o). If the Δ_o is increased, the configuration is more likely <u>low-spin</u>.

Now we can fill the <u>six</u> d-electrons into the crystal field diagram to find there are <u>no unpaired electrons</u>. This complex ion is diamagnetic.

1	1

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

1↓	1	1

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

high-spin (big Δ_o)

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

1↓	1↓	1↓

d_{xy} d_{yz} d_{xz}
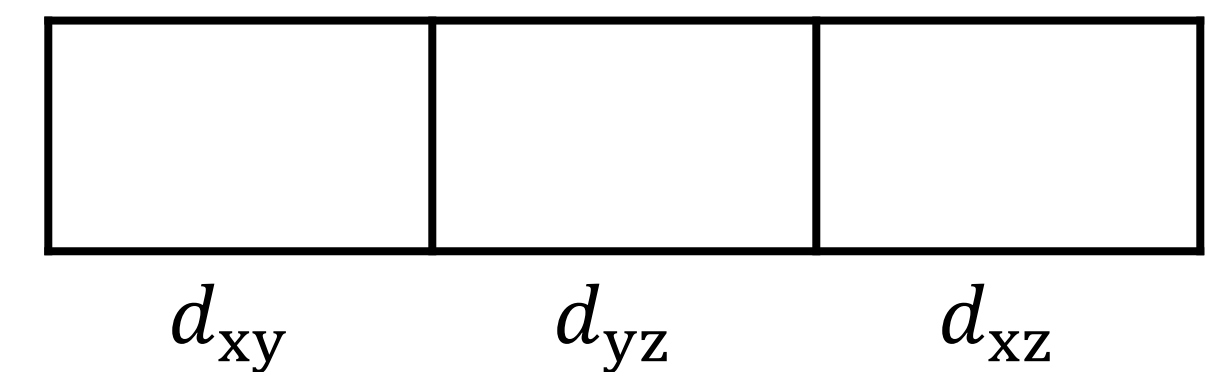
low-spin (big Δ_o)

PRACTICE PROBLEM 3

Calculate the magnetic moment for the two manganese complex ions: (a) $[Mn(CN)_6]^{4-}$ and (b) $[MnCl_6]^{4-}$.

Spectrochemical series: $CN^- > NO_2^- > CN^- > en > NH_3 > H_2O > F^- > Cl^- > Br^- > I^-$

Magnetic moment: $\mu_{\text{eff}} = \sqrt{n(n+2)}$

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

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

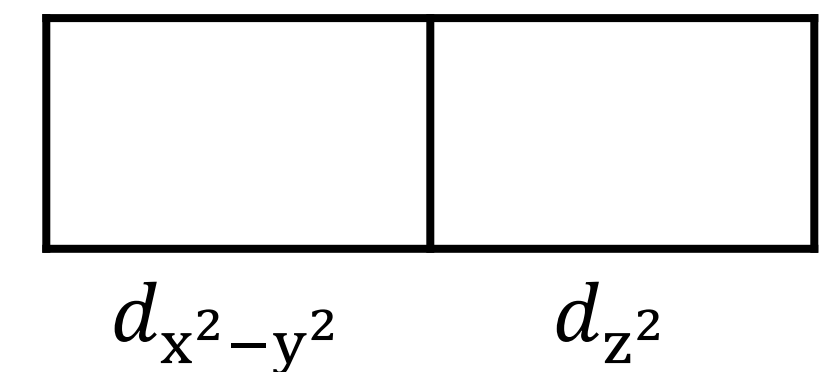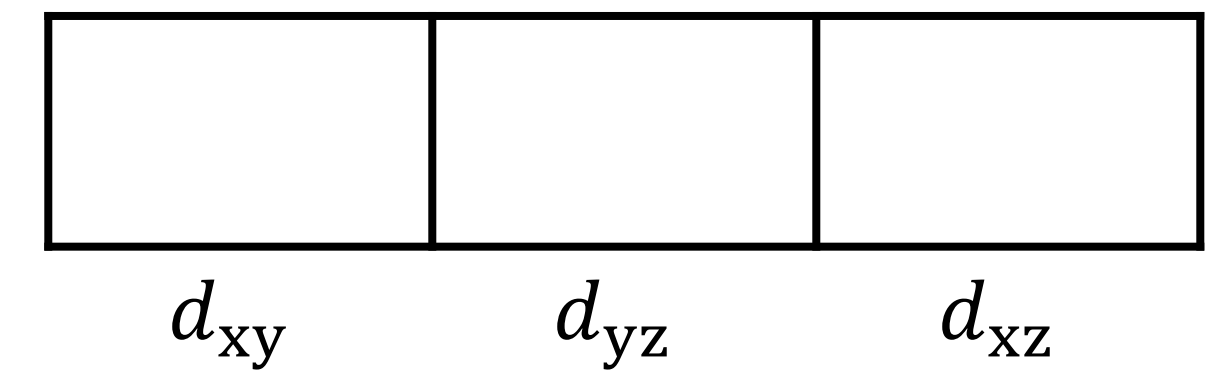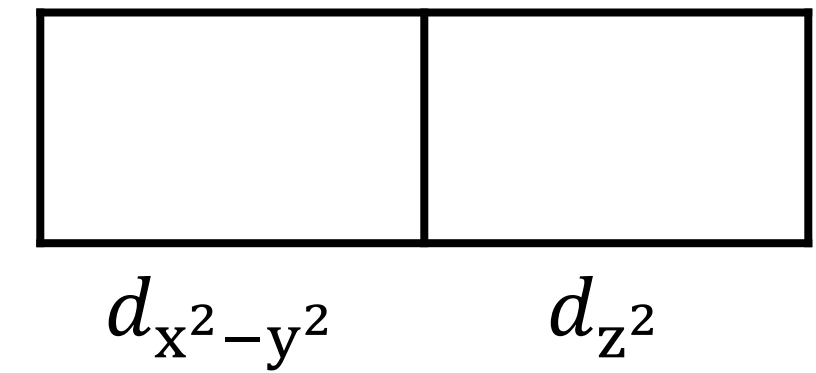|	
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Magnetic moment: $\mu_{eff} = \sqrt{n(n+2)}$

— answer —

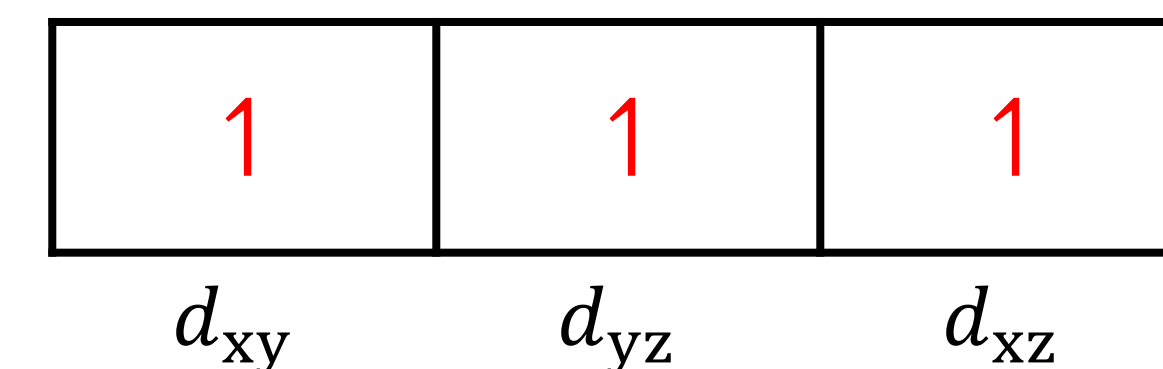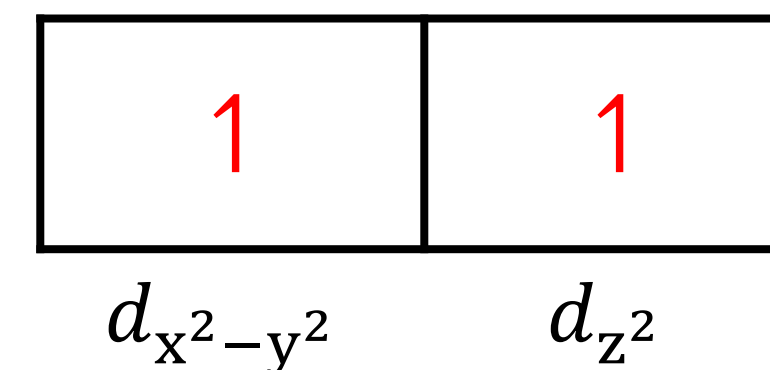First, determine the oxidation state of the metal center in both complexes: Mn(II).

Neutral Mn atom has an electronic configuration of $[Ar]4s^2 3d^5$; therefore, Mn^{2+} has an electronic configuration of $[Ar]3d^5$. This is a spin-ambiguous case because we can either have a high-spin or a low-spin configuration.

For (a), the ligand is CN^-, which is a <u>strong-field</u> ligand that <u>increases</u> the splitting energy (Δ_o), so the configuration is more likely <u>low-spin</u>. Therefore, n = 1 and

$$\mu_{eff} = \sqrt{1(1+2)} = 1.41 \ B.\,M.$$

For (b), the ligand is Cl^-, which is a <u>weak-field</u> ligand that <u>decreases</u> the splitting energy (Δ_o), so the configuration is more likely <u>high-spin</u>. Therefore, n = 5 and

$$\mu_{eff} = \sqrt{5(5+2)} = 5.92 \ B.\,M.$$

1	1

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

1	1	1

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

(b) → high-spin (big Δ_o)

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

1↓	1↓	1

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

(a) → low-spin (big Δ_o)

The UV-vis spectrum for the complex ion tris(1,10-phenanthroline)iron(II), $[Fe(phen)_3]^{2+}$, shows a maximum absorbance at 510 nm.

Estimate the energy splitting (Δ_o) for this complex ion.
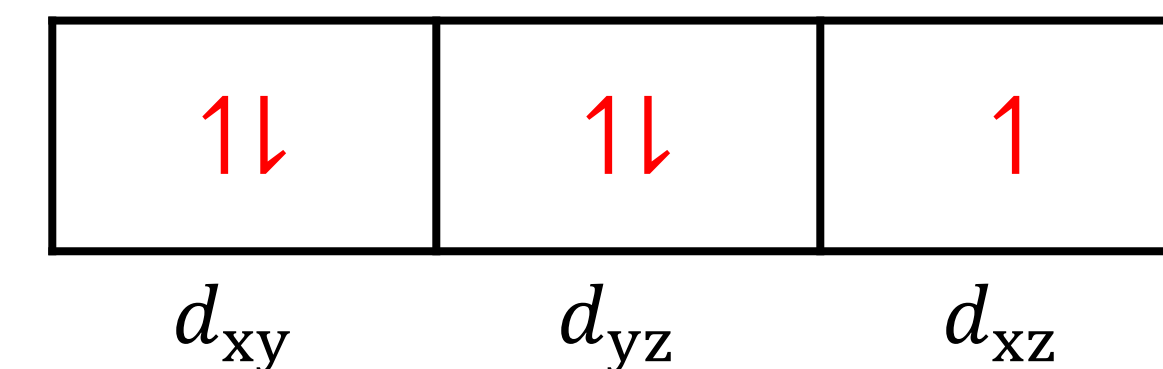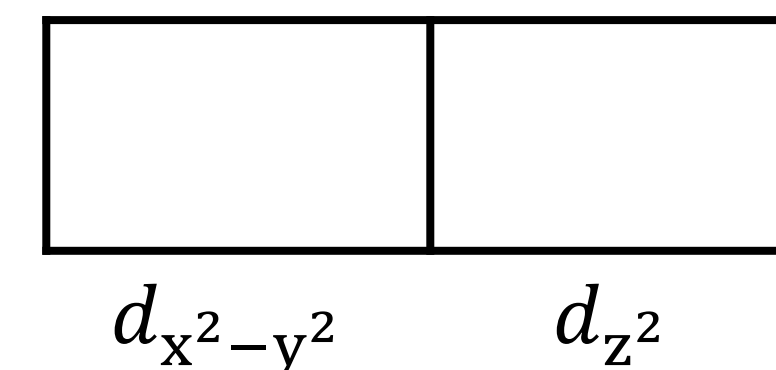
— answer —

PRACTICE PROBLEM 4

The UV-vis spectrum for the complex ion tris(1,10-phenanthroline)iron(II), $[Fe(phen)_3]^{2+}$, shows a maximum absorbance at 510 nm. Estimate the energy splitting (Δ_o) for this complex ion.

– answer –

Recall that the complementary color of the <u>observed color</u> of a complex is an indirect estimate of the energy splitting (Δ_o). As light passes through the solution, photons of a specific wavelength that is equal to the value of Δ_o are <u>absorbed</u> by the complex, while all other wavelengths of light are transmitted through the solution for our eyes to observe.

Therefore, the wavelength at the maximum absorbance can be used to estimate Δ_o via Planck's equation:

$$\Delta_o \approx E = \frac{hc}{\lambda_{max}} = \frac{\left(6.626 \times 10^{-34}\,\frac{J}{s}\right)\left(3.00 \times 10^8\,\frac{m}{s}\right)}{510 \times 10^{-9}\,m} = 3.90 \times 10^{-19}\,J$$

PRACTICE PROBLEM 5

Which of the two complex ions of iron would you expect to appear yellow?

$$[Fe(H_2O)_6]^{2+} \qquad or \qquad [Fe(CN)_6]^{4-}$$

Spectrochemical series: $CN^- > NO_2^- > CN^- > en > NH_3 > H_2O > F^- > Cl^- > Br^- > I^-$

— answer —

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

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

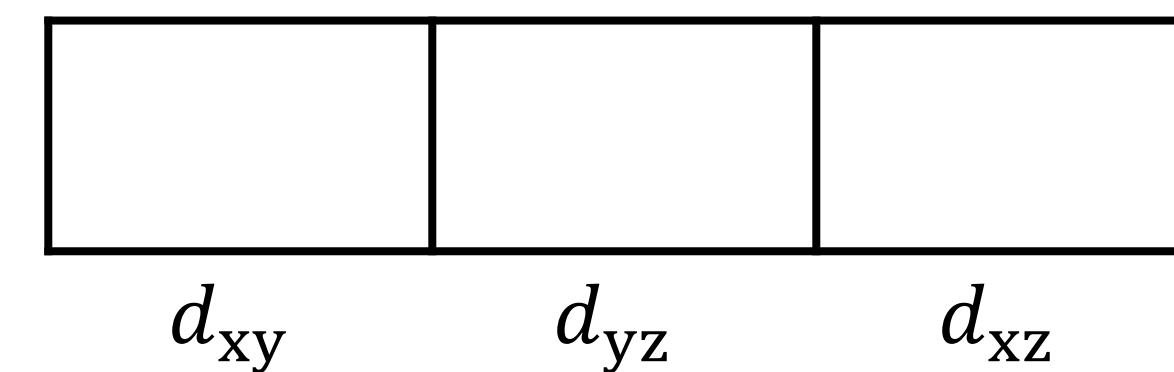| $d_{x^2-y^2}$	d_{z^2}

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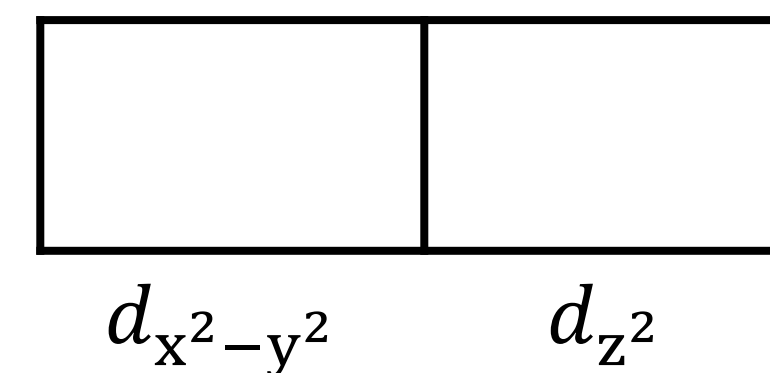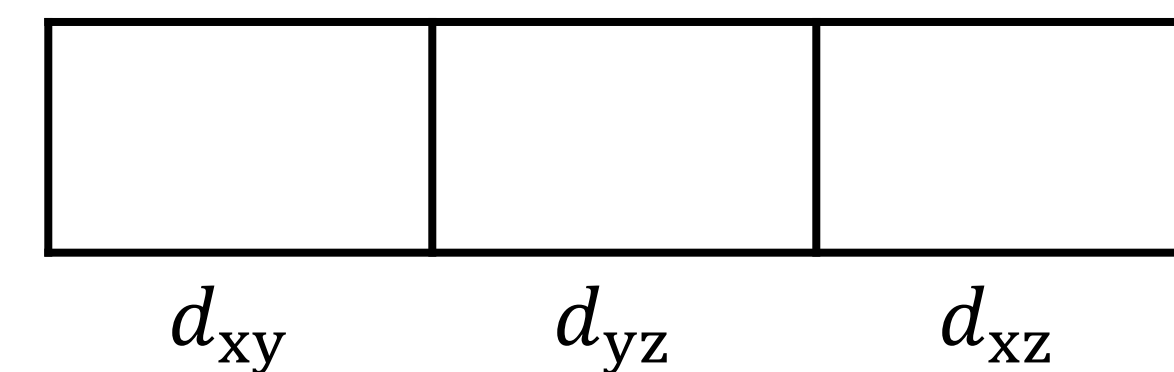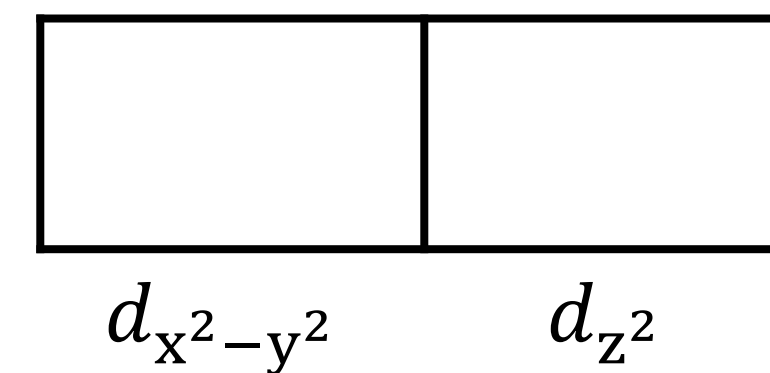
Spectrochemical series: $CN^- > NO_2^- > CN^- > en > NH_3 > H_2O > F^- > Cl^- > Br^- > I^-$

— answer —

First, determine the oxidation state of the metal center in both complexes: Fe(II).

Neutral Fe atom has an electronic configuration of $[Ar]4s^2 3d^6$; therefore, Fe^{2+} has an electronic configuration of $[Ar]3d^6$. This is a spin-ambiguous case because we can either have a high-spin or a low-spin configuration.

The CN^- ligand is a <u>strong-field</u> ligand that <u>increases</u> the splitting energy (Δ_o), so the configuration is more likely <u>low-spin</u>.

The H_2O ligand is a <u>weaker-field</u> ligand that <u>decreases</u> the splitting energy (Δ_o), so the configuration is more likely <u>high-spin</u>.

$[Fe(CN)_6]^{4-}$ is more likely to appear <u>yellow</u> because the value of Δ_o is larger, so it would absorb higher energy (violet) photons.

$d_{x^2-y^2}$	d_{z^2}
↑	↑

d_{xy}	d_{yz}	d_{xz}
↑↓	↑	↑

high-spin (big Δ_o)

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

d_{xy}	d_{yz}	d_{xz}
↑↓	↑↓	↑↓

low-spin (big Δ_o)