

Unit 3 – Deck 4

Inorganic

HSAB



Last Time

Introduction to Inorganic Coordination Chemistry

- Coordination Complexes
- Lewis Acids and Bases
- The Dative Bond
- Ions and Molecules as Ligands
- Coordination Complex Formation

Lecture Topics

- Equilibrium Constants of Coordination Complexes
- Chelate Effect
- Polydentate Ligands

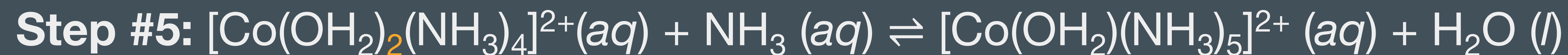
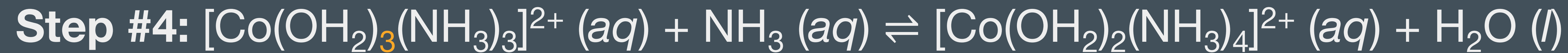
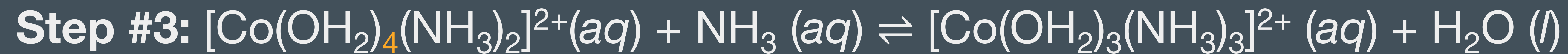
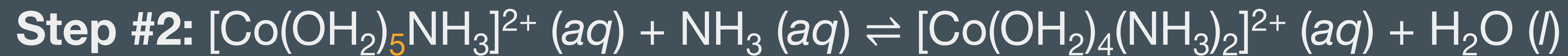
- Ionic Size and Charge
- **Hard and Soft Acid Base Theory**

Ligand Displacement

In coordination chemistry, ligands can be exchanged through a ligand displacement reaction.



Stepwise Displacement

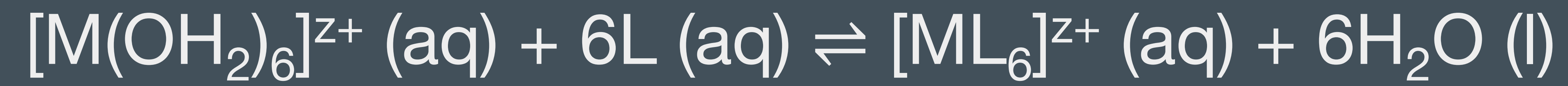


Example



What is K_{eq} for step 1?

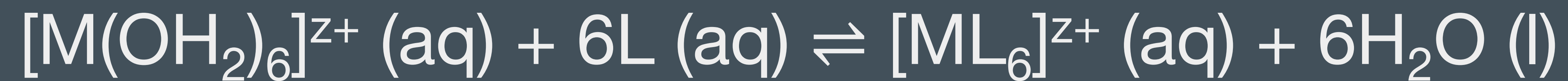
Example



$$K = \frac{[\text{ML}_6^{z+}]}{[\text{M}(\text{OH}_2)_6^{z+}][\text{L}]^6}$$

Trends in Equilibrium Constants

$$K = \frac{[ML_6^{z+}]}{[M(OH_2)_6^{z+}][L]^6}$$



log K

Number of Displaced H₂O Ligands

Enthalpy and Entropy in Complex Formation

When complex formation occurs (going from free metal cation and ligands to a ML_6 complex), the changes in enthalpy for these processes are significantly **negative**.

However, this change is accompanied by a significantly **negative** change in entropy.

Enthalpy and Entropy in Exchange

When ligand exchange occurs depending on the enthalpy change may be positive or negative. It depends on the relative bond strengths and solvation enthalpy of the ligands.

However, this change is accompanied by a significantly **positive** change in entropy (at least for the first few steps).

Complex Stability

Factor 1: Ionic size and magnitude of the charges.

The stability of a complex with a specific ligand increases substantially as the ionic charge increases. That is electrostatics predicts that bond strength should increase with the charge density of the cation.

This is only true if orbital interactions and polarizability can be ignored (very ionic compounds)

Stability of Oxidation States

Ionic radius decreases as the charge increases.

Li ¹⁺ 0.92 Å	Be ²⁺ 0.45 Å											H ¹⁻ 1.54 Å						B ³⁺ 0.27 Å	C ⁴⁺ 0.16 Å	N ³⁻ 1.46 Å	O ²⁻ 1.42 Å	F ¹⁻ 1.33 Å										
Na ¹⁺ 1.18 Å	Mg ²⁺ 0.89 Å																Al ³⁺ 0.54 Å	Si ⁴⁺ 0.40 Å	P ³⁺ 0.44 Å	S ²⁻ 1.84 Å	Cl ¹⁻ 1.81 Å											
K ¹⁺ 1.51 Å	Ca ²⁺ 1.12 Å	Sc ³⁺ 0.87 Å	Ti ³⁺ 0.67 Å	V ³⁺ 0.64 Å	Cr ²⁺ 0.80 Å	Mn ²⁺ 0.96 Å	Fe ²⁺ 0.92 Å	Co ²⁺ 0.90 Å	Ni ²⁺ 0.69 Å	Cu ²⁺ 0.73 Å	Zn ²⁺ 0.90 Å	Ga ³⁺ 0.62 Å	Ge ⁴⁺ 0.53 Å	As ³⁺ 0.58 Å	Se ²⁻ 1.98 Å	Br ¹⁻ 1.96 Å																
Rb ¹⁺ 1.61 Å	Sr ²⁺ 1.26 Å	Y ³⁺ 1.02 Å	Zr ⁴⁺ 0.84 Å	Nb ³⁺ 0.72 Å	Mo ⁴⁺ 0.65 Å	Tc ⁴⁺ 0.65 Å	Ru ³⁺ 0.68 Å	Rh ³⁺ 0.67 Å	Pd ²⁺ 0.86 Å	Ag ¹⁺ 1.28 Å	Cd ²⁺ 1.10 Å	In ³⁺ 0.92 Å	Sn ⁴⁺ 0.81 Å	Sb ³⁺ 0.76 Å	Te ²⁻ 2.21 Å	I ¹⁻ 2.20 Å																
Cs ¹⁺ 1.74 Å	Ba ²⁺ 1.42 Å	Hf ⁴⁺ 0.83 Å		Ta ³⁺ 0.72 Å	W ⁴⁺ 0.66 Å	Re ⁴⁺ 0.63 Å	Os ⁴⁺ 0.63 Å	Ir ³⁺ 0.68 Å	Pt ²⁺ 0.80 Å	Au ¹⁺ 1.37 Å	Hg ²⁺ 1.14 Å	Tl ³⁺ 0.98 Å	Pb ⁴⁺ 0.94 Å	Bi ³⁺ 1.17 Å	Po ⁴⁺ 1.08 Å	At ⁷⁺ 0.62 Å																
Fr ¹⁺ 1.80 Å	Ra ²⁺ 1.48 Å																															
																	La ³⁺ 1.16 Å	Ce ⁴⁺ 0.97 Å	Pr ³⁺ 1.13 Å	Nd ³⁺ 1.11 Å	Pm ³⁺ 1.09 Å	Sm ³⁺ 1.08 Å	Eu ³⁺ 1.07 Å	Gd ³⁺ 1.05 Å	Tb ³⁺ 1.04 Å	Dy ³⁺ 1.03 Å	Ho ³⁺ 1.01 Å	Er ³⁺ 1.00 Å	Tm ³⁺ 0.99 Å	Yb ³⁺ 0.98 Å	Lu ³⁺ 0.98 Å	
																	Ac ³⁺ 1.12 Å	Th ⁴⁺ 1.05 Å	Pa ⁵⁺ 0.78 Å	U ⁶⁺ 0.52 Å	Np ⁵⁺ 0.75 Å	Pu ⁴⁺ 0.96 Å										

*The effects of size and charge reinforce each other, leading to **greater stability** for complexes involving the higher oxidation state metal.*



Complex Stability



Factor 2: Stability of the complex depends on the parity of orbital radius and magnitude of orbital overlap between metal ion (e^- acceptor / Lewis acid) the and ligands (e^- donor / Lewis base).

Hard acids (hard metal cations) form more stable complexes with **hard bases** (hard ligands).

Soft acids (soft metal cations) show a preference for **soft bases** (soft ligands).

Hard vs. Soft Acids (metals)

Hard acids have high charge densities and small valence orbitals

- Not very polarizable
- Attracted to ligands that are not very polarizable
- Examples: Cr^{3+} , Zr^{4+} , Al^{3+}

Soft acids are prototypically large cations with low charge densities

- Very polarizable
- Interact with ligands that are also very polarizable
- Examples: Cu^+ , Ag^+ , Au^+

Hard vs. Soft Bases (ligands)

Hard/Soft Ligands are categorized by their electronegativities and polarizability



Hard
Ligands

Soft
Ligands

Ligand oxidation state / hybridization can lead to very different 'hardness'

Ammonia vs Nitride

Example

$F > O > N > Cl > Br > C \approx I \approx S > Se > P > As > Sb$
(Hard to Soft Ligands)

Hard Acid

(Small Atom & High Charge)



Soft Acid

(Large Atom & Small Charge)



Metal Ion	$\log_{10} K_{eq}$			
	X = F	X = Cl	X = Br	X = I
Fe^{3+}	6.0	1.4	0.5	-
Hg^{2+}	1.0	6.7	8.9	12.9

General Trends

Ligands with **hard donor** atoms (e.g. O and N) form more stable complexes with *light cations and high charge*.

- s-block: Na^+ , Mg^{2+}
- p-block: Al^{3+}
- d-block: Sc^{3+} , Cr^{3+} , Fe^{3+}
- f-block: Ce^{3+} , Th^{4+}

Ligands with **soft donor** atoms (e.g. S and P) show a preference for heavy *metal ions and small charge*. Mutual polarization and covalence is a more important driving force.

- p-block: Tl^+
- d-block: Cu^+ , Ag^+ , Hg^{2+}

Common Ligands & Metals

Ligands

Metals

Hard

F⁻, Cl⁻, H₂O, alcohols, ethers, OH⁻, alkoxide, carboxylate, CO₃²⁻, NO₃⁻, PO₄⁻, SO₄²⁻, ClO₄⁻, oxalate, NH₃, & organic amines

Li⁺, Na⁺, K⁺, Rb⁺, Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺, Sn²⁺, Mn²⁺, Zn²⁺, Al³⁺, Ga³⁺, In³⁺, Sc³⁺, Cr³⁺, Fe³⁺, Co³⁺, Y³⁺, Th⁴⁺, Pu⁴⁺, Ti⁴⁺, Zr⁴⁺, [VO]⁺, & [VO₂]⁺

Soft

I⁻, H⁻, alkyl anion (R:⁻), CN⁻, CO, isocyanide (R-NC), thiol (R-SH), thioethers (RSR), thiolate (R-S⁻), thiocyanate (-SCN), phosphines R₃P, arsines R₃As, Stibene R₃Sb, alkene, arene

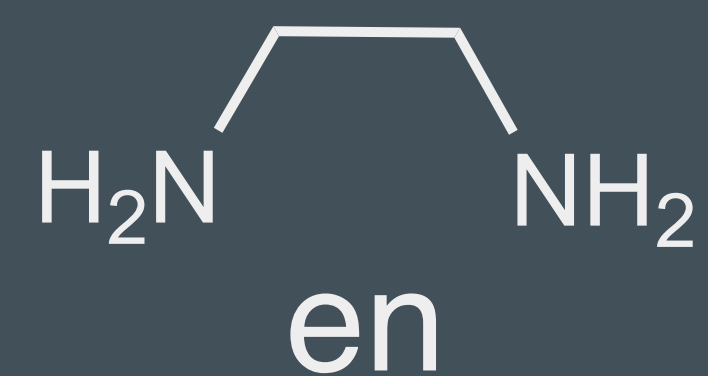
Al, Cu, Zn, Ga, Cr, Fe, Hg, Ag, Au, Tl⁺, Cu⁺, Ag⁺, Au⁺, [Hg₂]⁺, Hg²⁺, Cd²⁺, Pd²⁺, Pt²⁺, & Tl³⁺

Intermediate

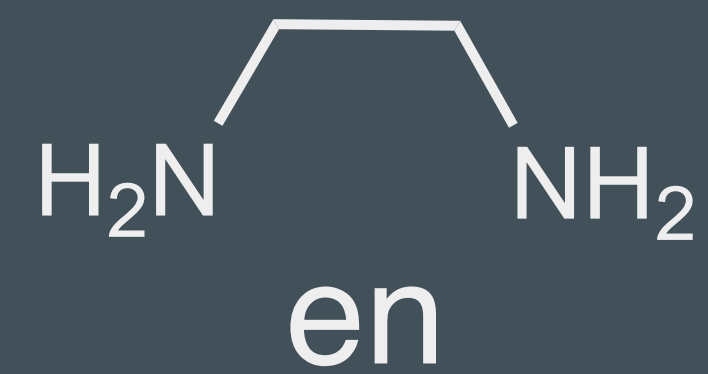
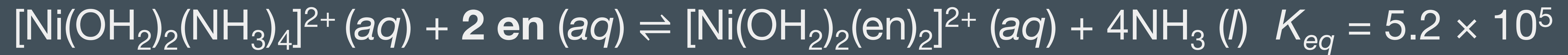
Br⁻, N₃⁻, pyridine, aniline (Ph-NH₂), NO₂⁻, & SO₃²⁻

Pb²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Os²⁺, Ru³⁺, Rh³⁺, & Ir³⁺

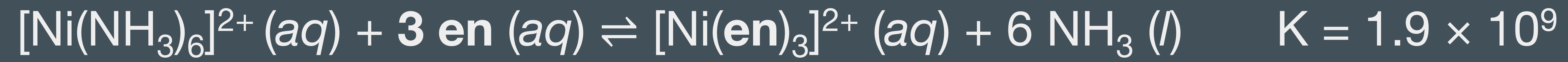
Bidentate Ligands



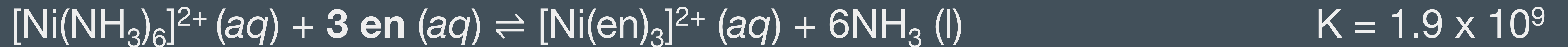
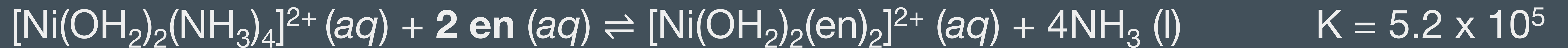
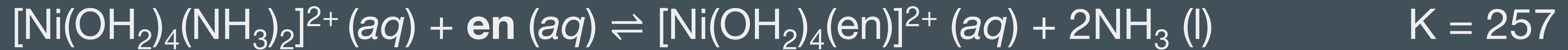
Example – two equiv. of ethylenediamine (en)



Example

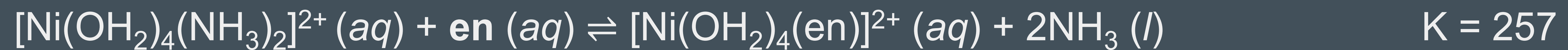


Entropy and K



Chelate Effect

A chelate more thermodynamically stable than that of a complex containing a corresponding number of comparable monodentate ligands. This is called the *chelate effect*.



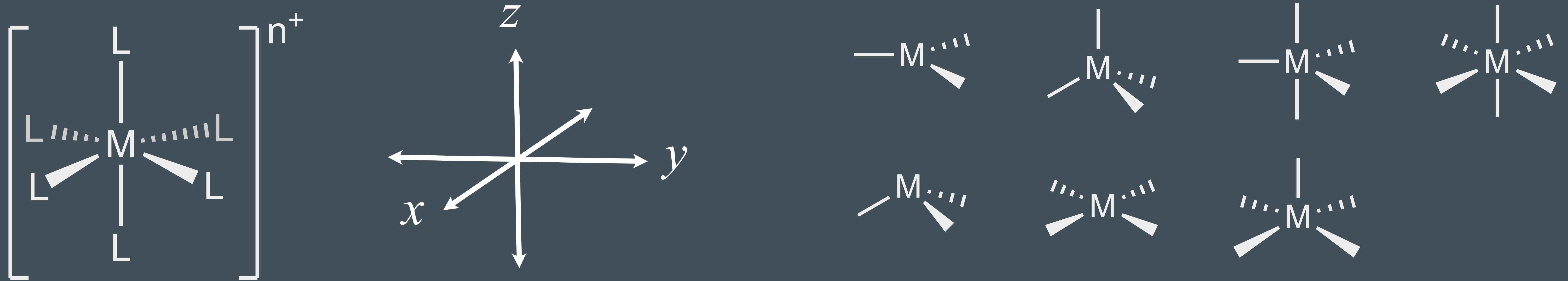
Stability Theories That Help Explain the Chelate Effect

1. Entropy driven: $\Delta G = \Delta H - T\Delta S$

Other factors to consider:

2. A reduction in the electrostatic repulsion between the donor atoms going from two monodentate ligands to one bidentate ligand.
3. Desolvation effects involving the disruption of hydrogen bonds between the water ligand and the solvent
4. An inductive effect of the backbone bridges in polydentate ligands which increase the donor strength of the ligand with respect to a corresponding monodentate ligand
5. A proximity effect. The after one part of bidentate ligand binds the other donor is statistically much closer to the metal than any other free monodentate ligand in solution. Thus it is more likely to interact and coordinated to the metal center.

3-D Shape of Complexes



We'll focus on the octahedral coordination geometries

d-orbitals Review

d-orbitals are characterized by the quantum number $\ell = 2$

For $\ell = 2$, there are only five degenerate harmonics that satisfy the Schrödinger equation:

$$m_\ell = +2, +1, 0, -1, -2$$

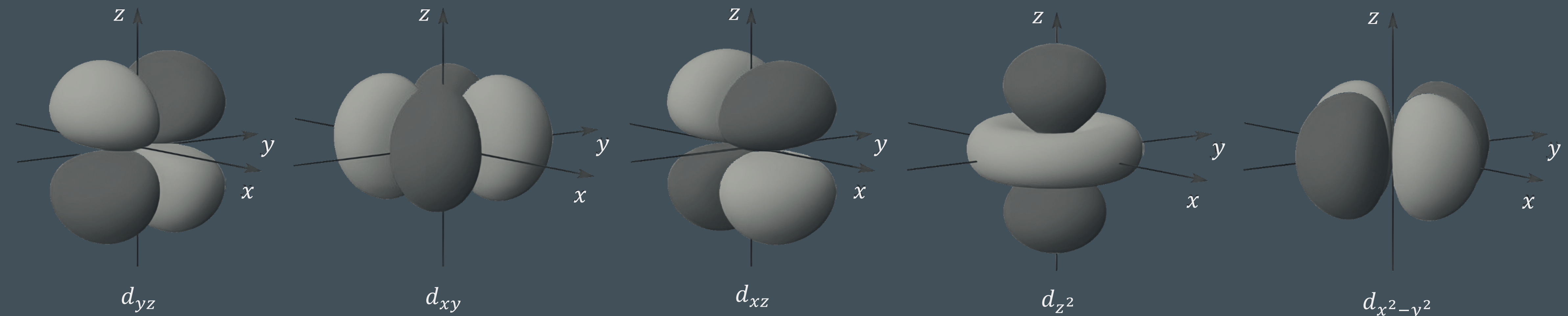
These are complex functions. However, using the principal of superposition we can take linear combinations of these m_ℓ wavefunctions (physics) to get a set of 5 other wavefunctions that evaluate as purely real numbers.

These are:

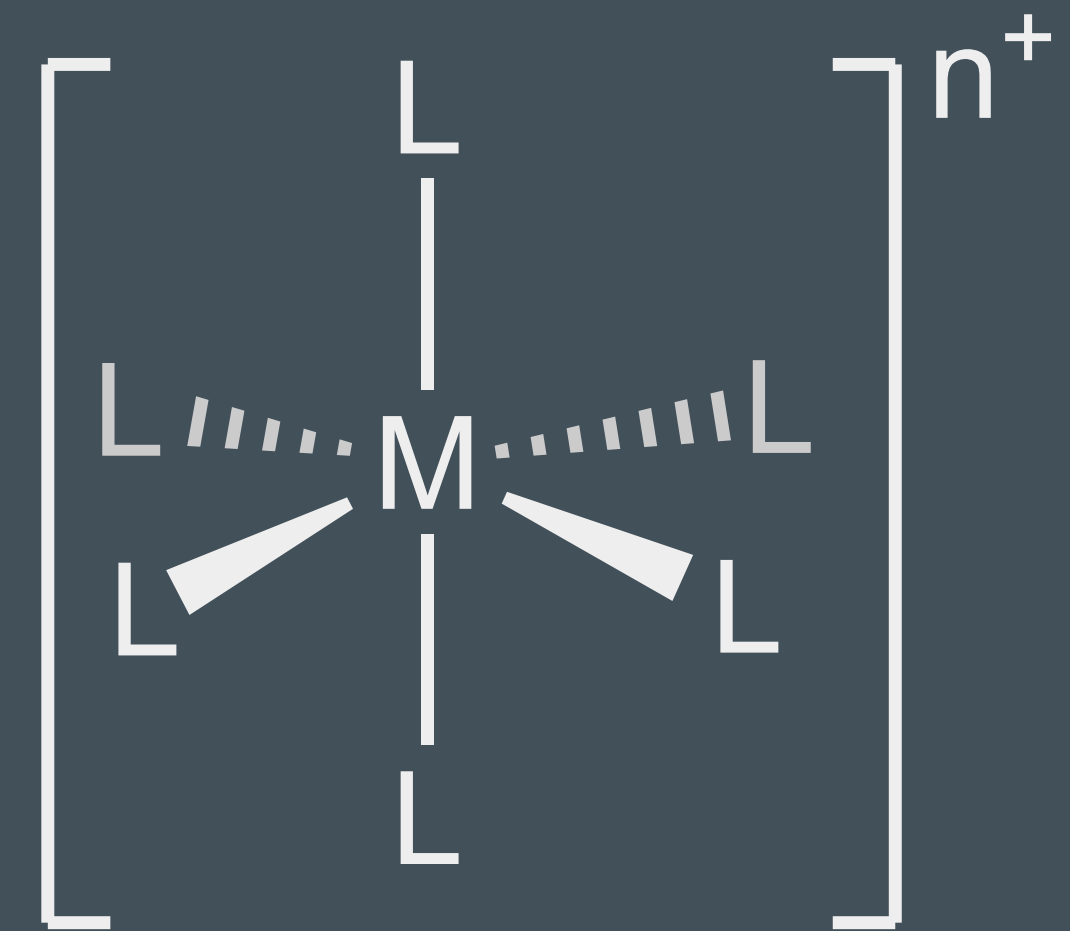
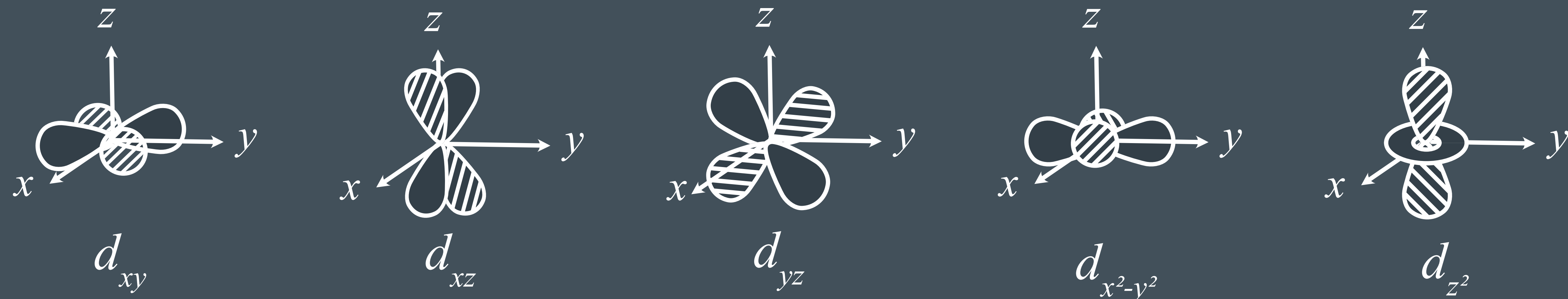
The 5 chemistry *d*-orbitals: d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$, and d_{z^2}

Plotting and drawing the d -orbitals

3D Render

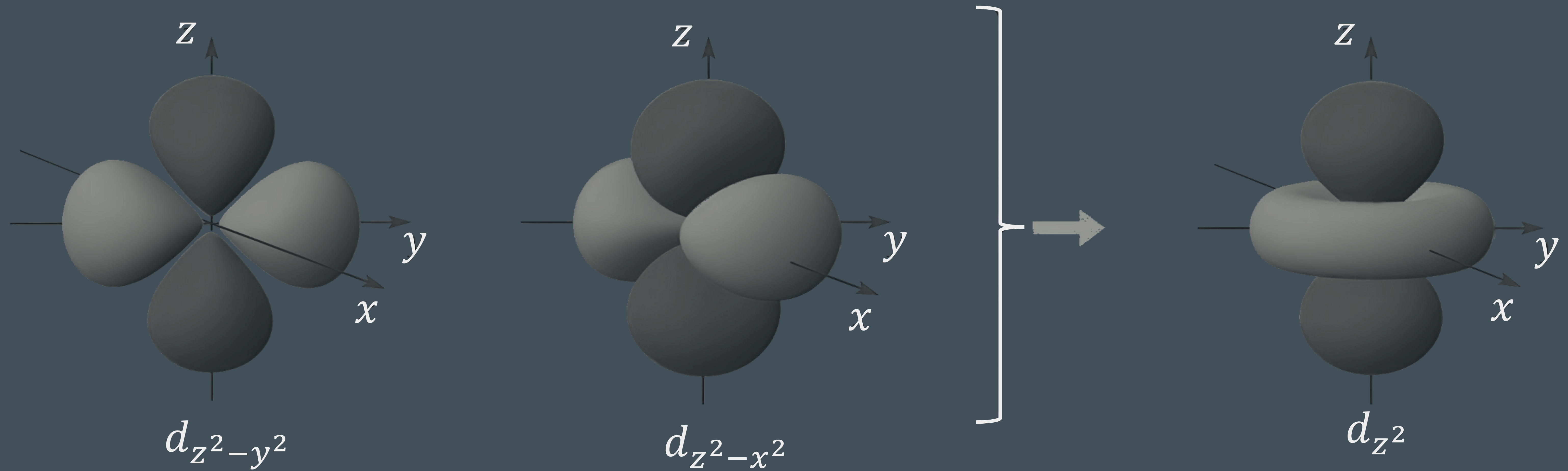


Drawing them by hand



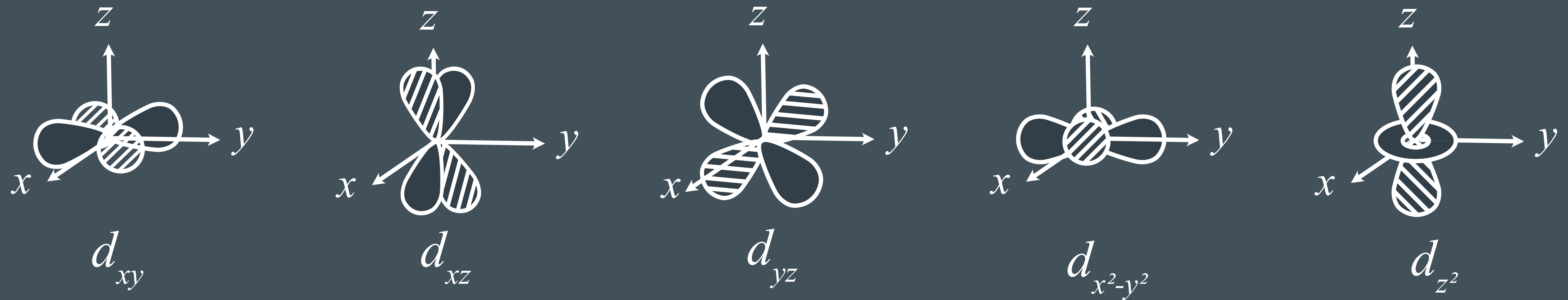
Take careful note of the orientations with respect to the axes!

The d_{z^2} -orbital looks different



This is not a p -orbital!

Orbital Notation for d -orbitals



Recall: Transition metals don't necessarily follow strict electron count rules like the octet rule for carbon. They are more complicated!

Odd electron counts and unpaired electrons in even electron counts are common!

Basics of Magnetism – Unpaired electrons

Magnetic data for d^6 octahedral complexes show that there are two main categories.

1. **Paramagnetic:** complexes with at least one unpaired electron
2. **Diamagnetic:** complexes with no unpaired electrons

Example

Experimental data also suggests that there are two magnetic categories for d^4 , d^5 , and d^7 octahedral complexes.

Unlike d^6 , these complexes are ALL paramagnetic. The only difference is that they have a different number of unpaired electrons.

Next Time

- Valence Bond Theory (atomic orbital hybridization schemes)
- Crystal Field Theory
- High-Spin States & Low-Spin
- Octahedral Field Splitting
- Crystal Field Stabilization Energy