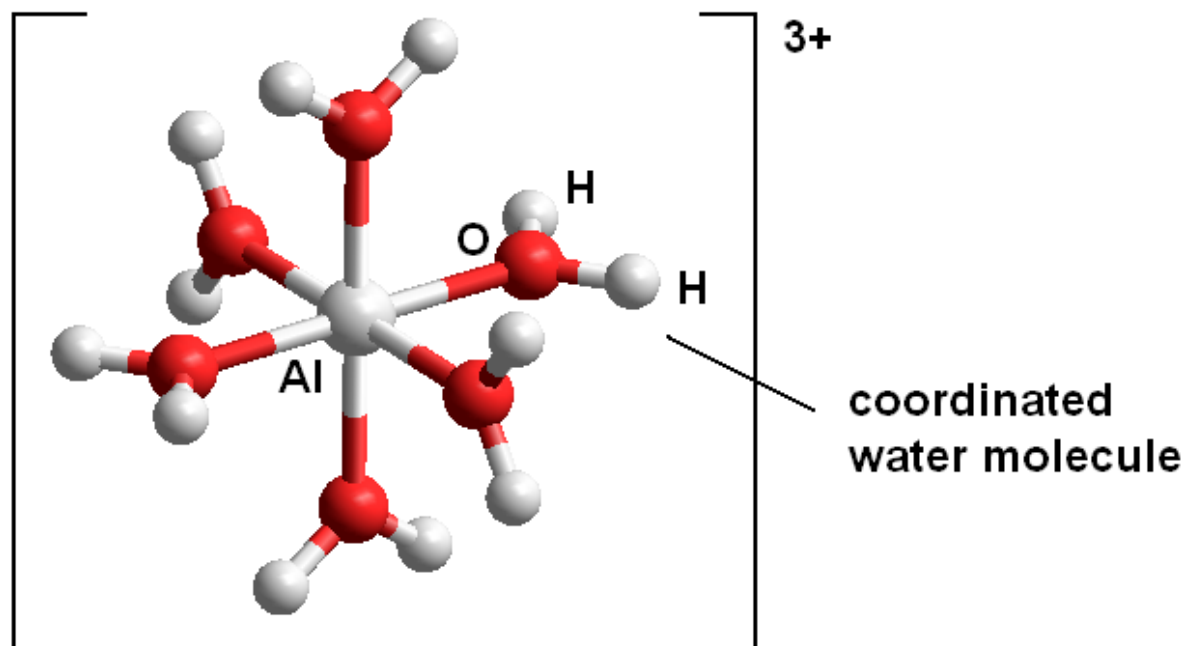
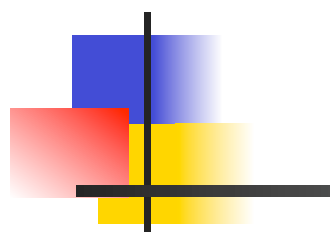


The hydrolysis of metal ions in aqueous solution.



Metal aqua ions:

Metal ions in aqueous solution exist as aqua ions, where water molecules act as ligands, and coordinate to the metal ion via the oxygen donor atoms as shown for the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ hexaaqua ion below:

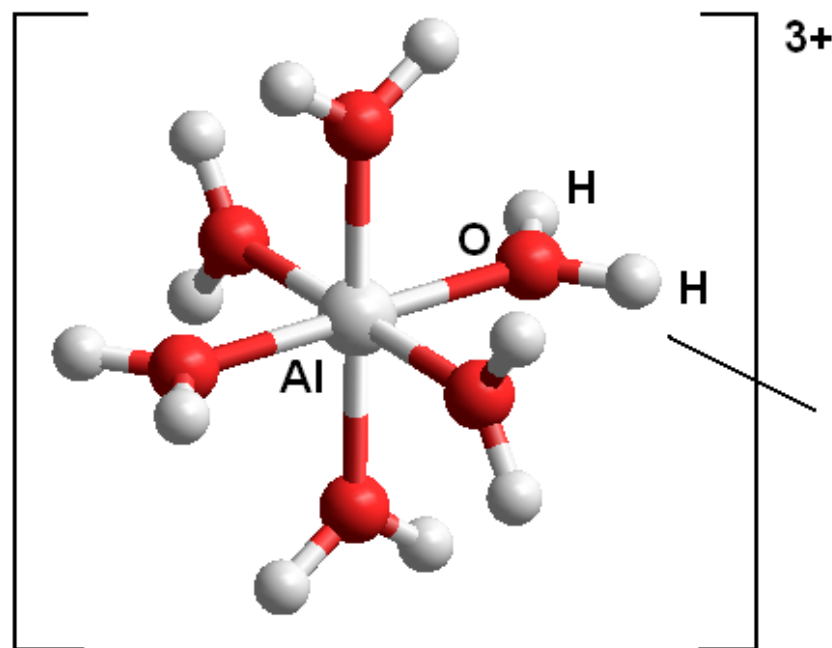


Figure 1. The aluminum(III) hexaaqua ion, present in aqueous solution and in many salts such as $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$, often written as $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$.

coordinated
water molecule

Metal ions can have varying numbers of water molecules coordinated to them, ranging from four for the very small Be(II) ion, up to 9 for the large La(III) ion. These are shown in Figure 2.

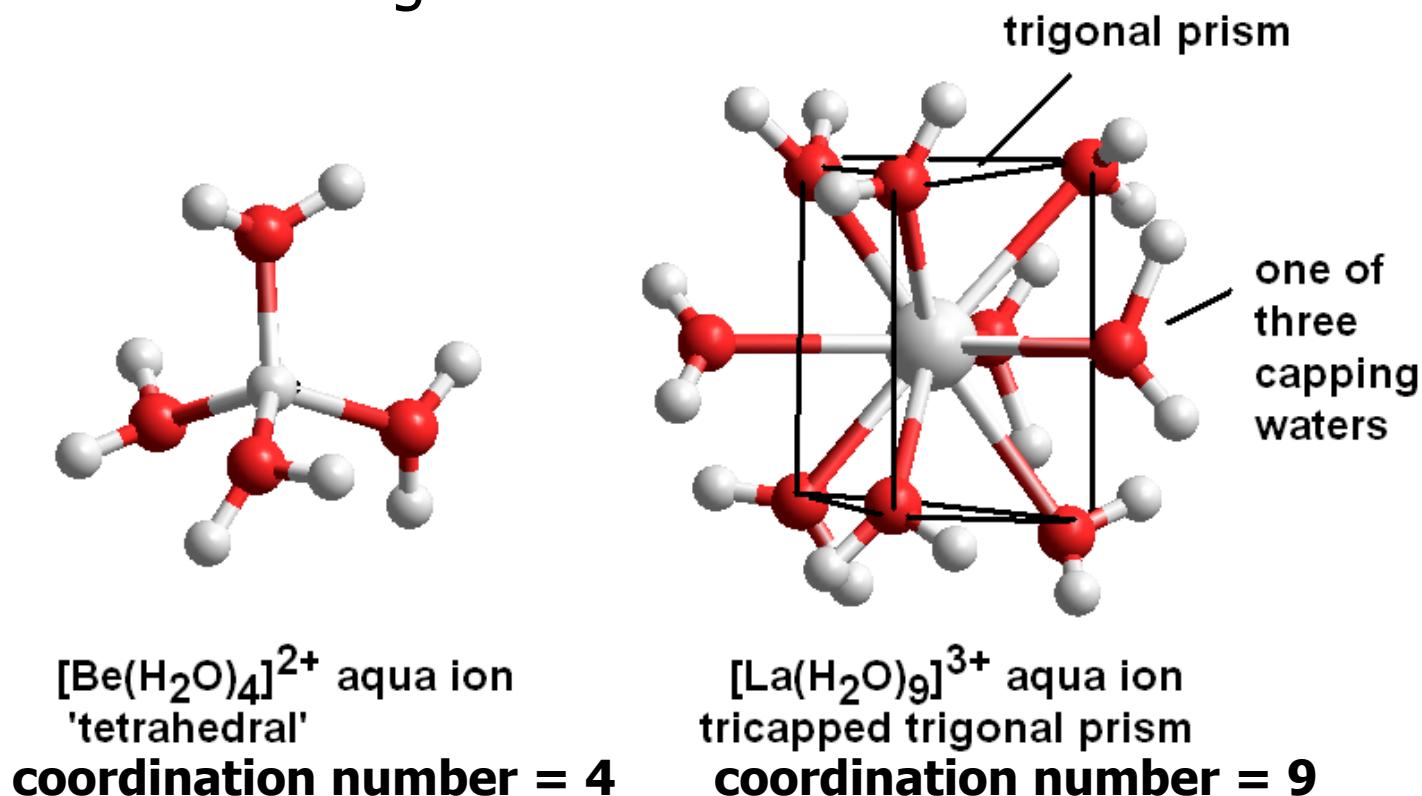
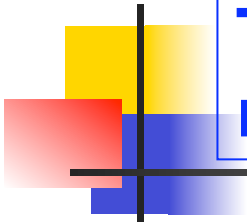


Figure 2. The Be(II) and La(III) aqua ions, Be(II) generated using PM3, the La(III) is from the CSD (Cambridge Structural Database)¹, entry number SUDDAW. As shown, the geometry around the La^{3+} is a tricapped trigonal prism, a common geometry for nine-coordinate species with unidentate ligands.



The inner and outer sphere of waters around metal ions in solution:

In the solid state, the H-atoms of the coordinated waters are almost always H-bonded to other waters, or anions such as nitrate or perchlorate. In aqueous solution, this H-bonding structures the water molecules around the aqua ion into what is called the 'outer-sphere' of solvating water molecules, while the water molecules coordinated directly to the metal ion are referred to as the 'inner-sphere' waters. This is illustrated for the Al(III) aqua ion below, where each H-atom from an inner-sphere water has a water molecule H-bonded to it, giving twelve water molecules in the outer-sphere:

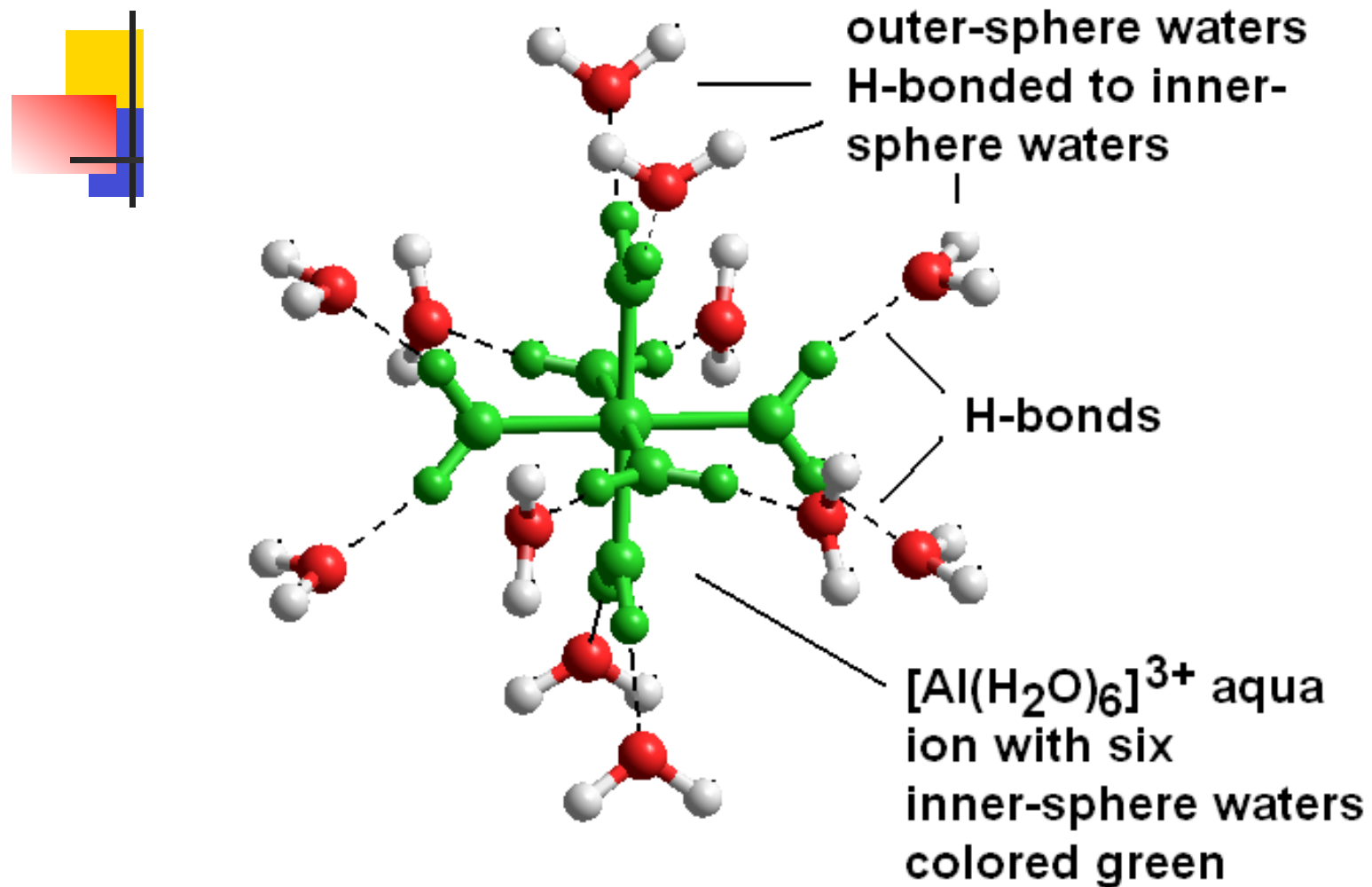
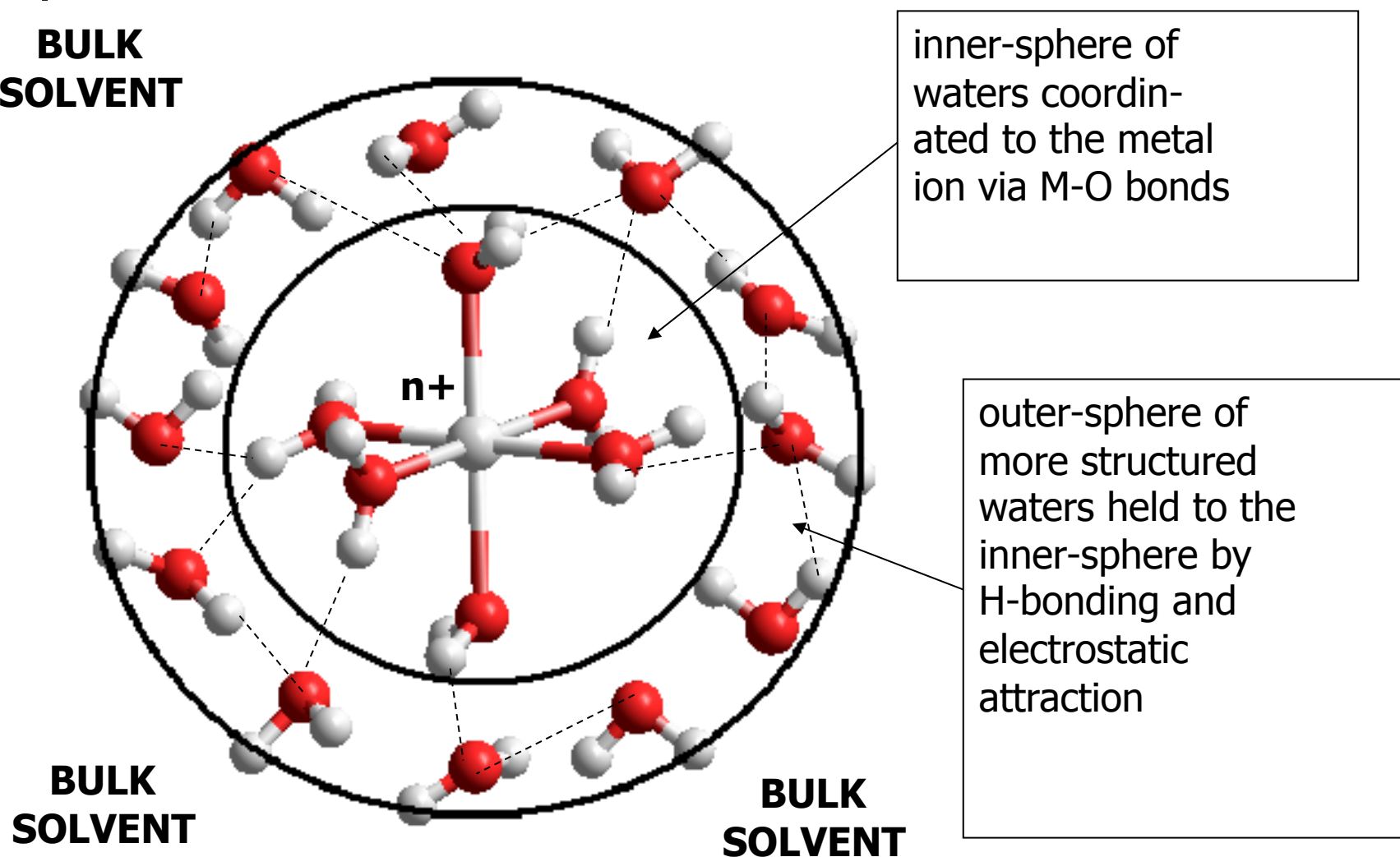


Figure 3. The Al(III) aqua ion showing the six inner-sphere waters (colored green) and twelve outer-sphere waters H-bonded to the inner-sphere.

Diagrammatic representation of the inner and outer sphere of waters around a metal ion in solution:

**BULK
SOLVENT**



A point of interest is that water can exist also as a bridging ligand, as in numerous complexes such as those

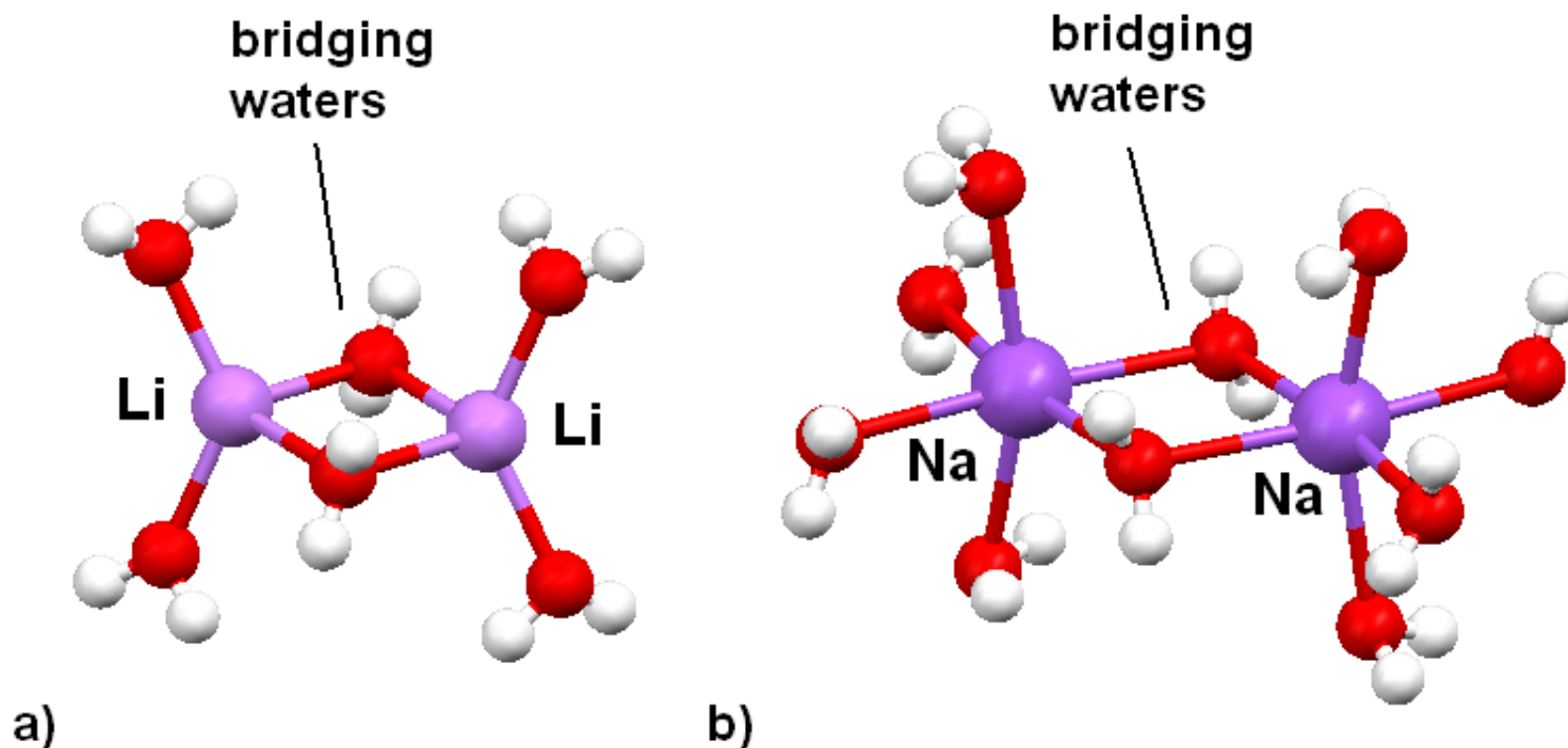
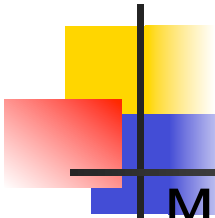
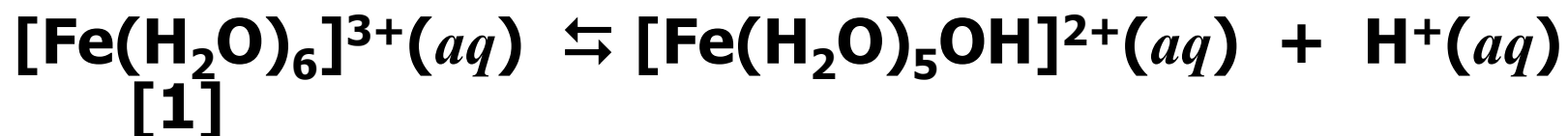


Figure 4. Bridging waters as found in a) the $[\text{Li}_2(\text{H}_2\text{O})_6]^{2+}$ cation (CSD = CELGUV) and b) the $[\text{Na}_2(\text{H}_2\text{O})_{10}]^{2+}$ cation (CSD = ECEPIL).

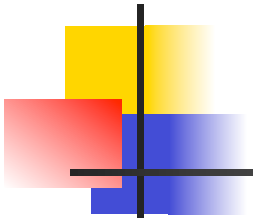


Metal aqua ions as Brønsted acids:

Metal aqua ions can act as Brønsted acids, which means that they can act as proton donors. Thus, an aqua ion such as $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is a fairly strong acid, and has² a $\text{p}K_{\text{a}}$ of 2.2. This means that the equilibrium constant for the following equilibrium has a value of $10^{-2.2}$.



Thus, if one dissolves a ferric salt, such as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in water, a fairly acidic solution of pH about 2 will result. In fact, the orange color of such solutions is due to the presence of the $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ ion, and the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ cation is actually a very pale lilac color. The latter color can be seen in salts such as $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, which contains the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ cation.



The formation constant (K):

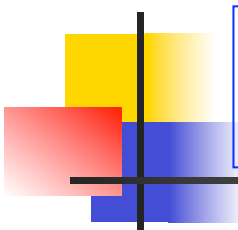
The formation constant (K_1) is a measure of the stability of a complex (ML) formed by a metal ion (M) with a ligand (L) in aqueous solution, and refers to the equilibrium:



The constant is expressed as:

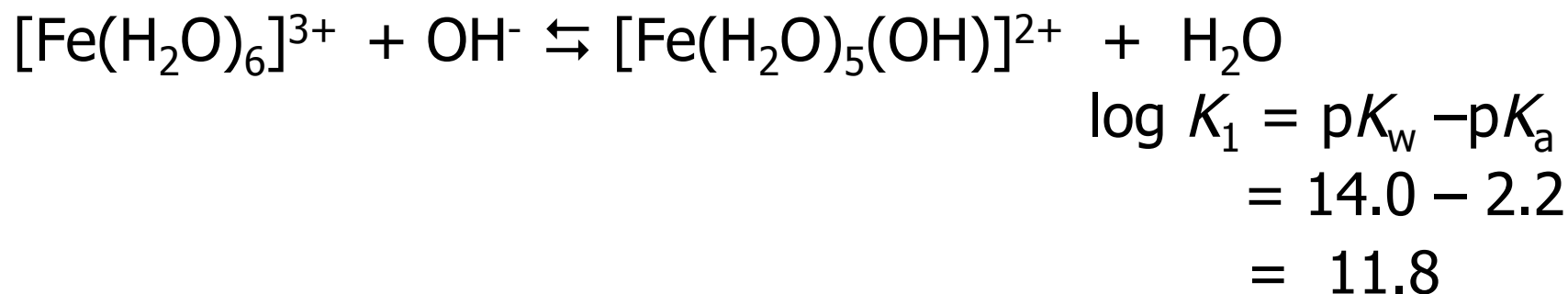
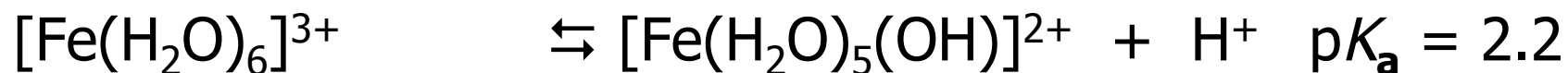
$$K_1 = \frac{[\text{ML}]}{[\text{M}][\text{L}]}$$

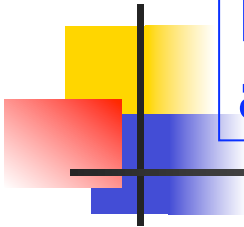
K values are usually rather large, and so are usually given as $\log K$ values.



Formation constants (K_1) of metal ions with hydroxide:

As already mentioned, the hydroxide ion is a ligand. So when, for example, $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ is formed, we can regard this as replacement of a coordinated water by hydroxide, rather than as loss of a proton. The two equations are related as follows:



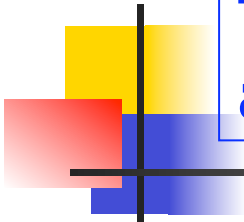


Factors that control the acidity of metal ions in aqueous solution:

Metal aqua ions display varying pK_a values that are dependent on size, charge, and electronegativity.

1) **The smaller the metal ion**, the more acidic it will be. Thus, we have for the group 2 metal ions the following pK_a values (note that ionic radii³ increase down a group):

					
	increasing metal ion acidity increasing metal ion size				
Metal ion:	Be ²⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺
Ionic radius (Å):	0.27	0.74	1.00	1.18	1.36
pK_a :	5.6	11.4	12.7	13.2	13.4
$\log K_1(\text{OH}^-)$	8.4	2.6	1.3	0.8	0.6



The effect of the charge on the metal ion on acidity:

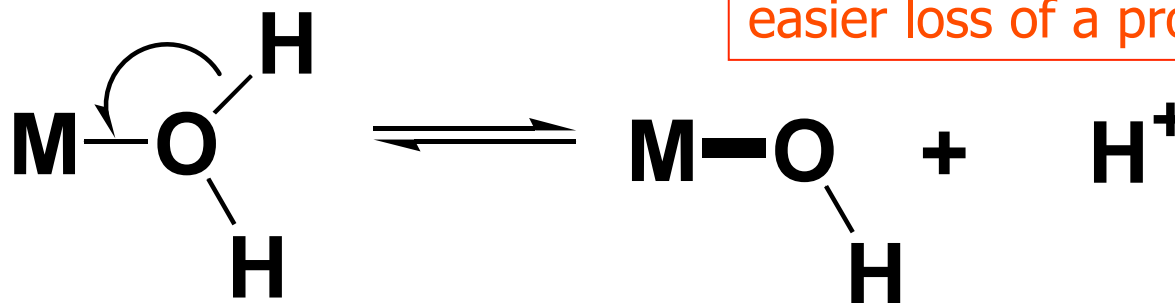
The higher the charge on metal ions of about the same size, the more acidic will the metal ion be:

					increasing metal ion charge
Metal ion:	Na ⁺	Ca ²⁺	La ³⁺	Th ⁴⁺	
Ionic radius (Å):	1.02	1.00	1.03	0.94	
pK _a :	14.1	12.7	8.5	3.2	
Log K ₁ (OH ⁻):	-0.1	1.3	5.5	10.6	
					increasing metal ion acidity

The effect of electronegativity of the metal on the acidity of its aquo ion:

3) **Electronegativity.** This was discussed in lecture 5, but is repeated here briefly as a reminder. The closer a metal is to Au in the periodic table, the higher will its electronegativity be. Electronegativity tends to override the first two factors in controlling the acidity of metal aqua ions, and metal ions of higher electronegativity will be much more acidic than metal ions of similar size and charge, but of low electronegativity.

metal ion forms stronger M-O bond and pulls electron density from the O-H bond



reduced electron density in O-H bond leads to easier loss of a proton:

Electronegativities of the Elements

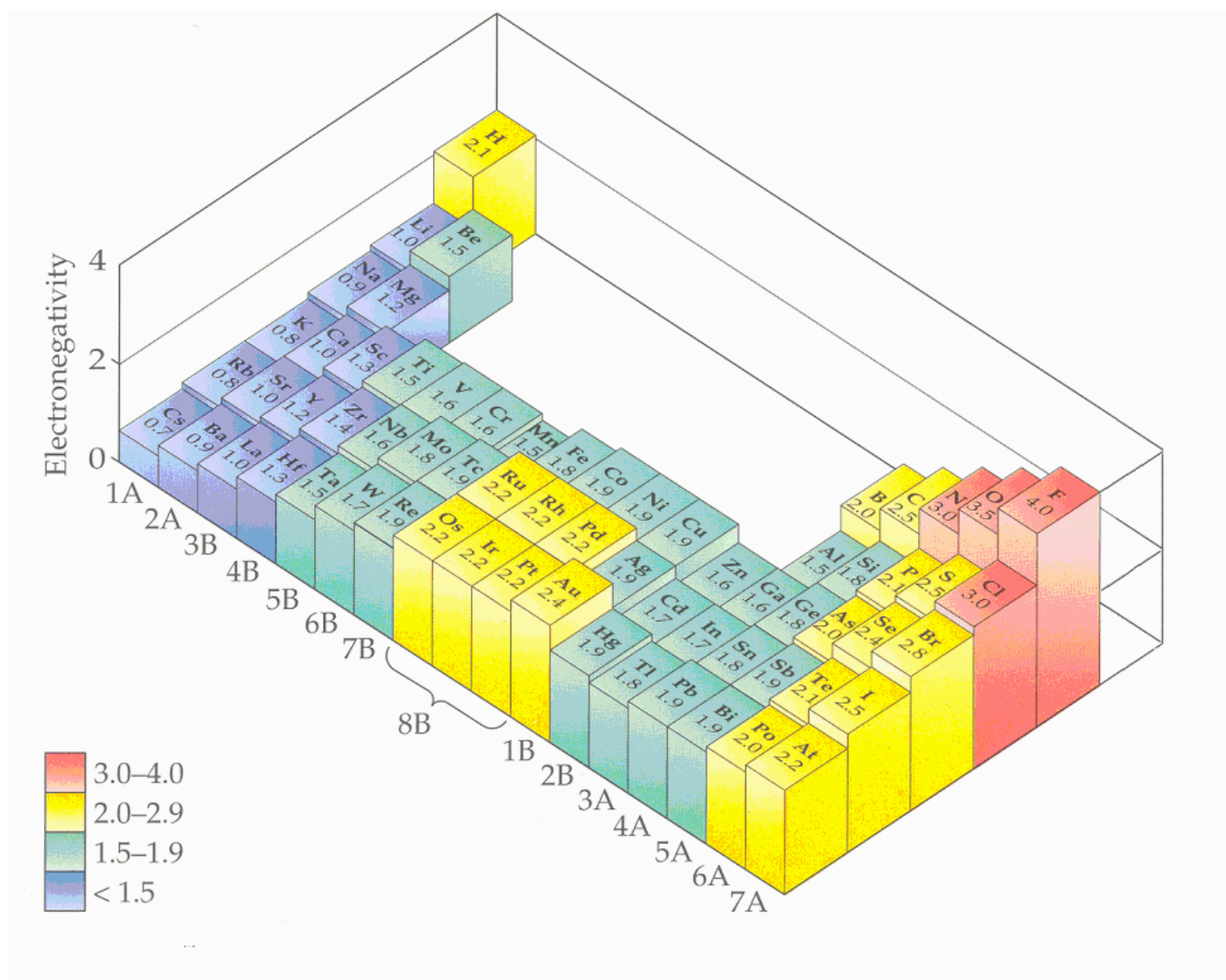


Figure 5. Electronegativities of the elements.

Thus, one sees that Pb^{2+} has a high electronegativity (E.N.) of 1.9, while the similarly sized and charged Sr^{2+} will have a low E.N. of 1.0, and consequently much lower acidity. Similar results are observed for other pairs of metal ions such as Ca^{2+} and Hg^{2+} (these results can be rationalized by referring to the above periodic table in Figure 5):

Metal ion:	Sr^{2+}	Pb^{2+}	Ca^{2+}	Hg^{2+}
Ionic radius (Å):	1.19	1.18	1.00	1.02
E.N.	1.0	1.9	1.0	1.9
pK_a	13.2	8.0	12.7	3.4
$\log K_1(\text{OH}^-)$	0.8	6.0	1.3	10.6

Higher electronegativity

Higher acidity/affinity for OH^-

Species distribution diagrams for metal ions:

One finds, as for acids such as CH_3COOH , that metal ions are 50% hydrolyzed at the pH that corresponds to their $\text{p}K_a$. This can be summarized as a species distribution diagram as shown below:

Cu(II) species distribution diagram

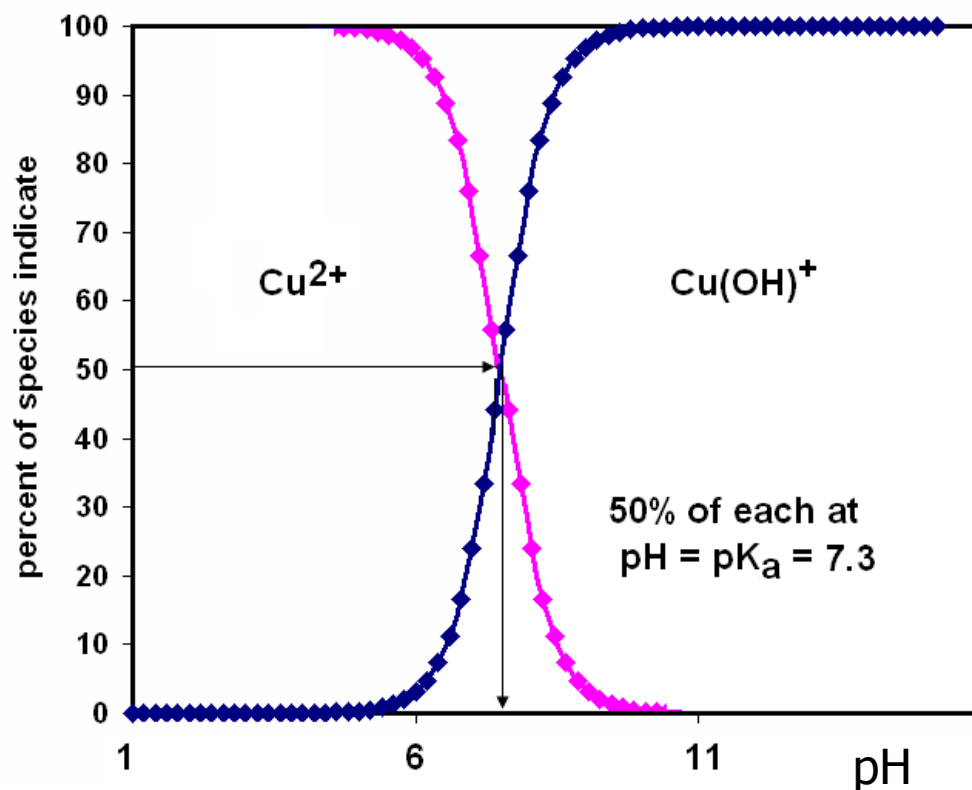
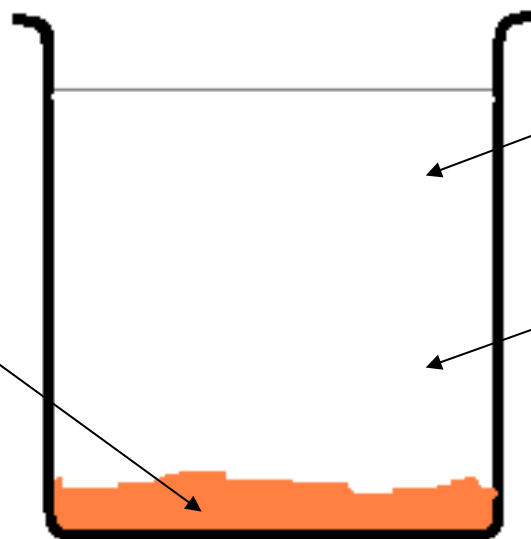


Figure 6. Species distribution diagram for Cu(II) in aqueous solution. Other solution species such as $[\text{Cu}(\text{OH})_2]$ have been ignored in calculating the diagram. Note that the concentrations of Cu^{2+} and $\text{Cu}(\text{OH})^+$ are equal at a pH equal to the $\text{p}K_a$ of 7.3. Note that $\log K_1(\text{OH}^-)$ for Cu(II) = $14 - 7.3 = 6.7$.

Solubility of metal hydroxides and amphoteric behavior.

$$K_{so} = [\text{Fe}^{3+}] [\text{OH}^-]^3 = 10^{-39}$$

$\text{Fe}(\text{OH})_3 (s)$
precipitate



pH = 6.4

$[\text{Fe}^{3+}] = 10^{-16} M$



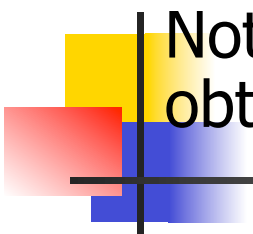
Solubilities of metal hydroxides.

If one leaves an orange solution of a ferric salt to stand, after a while it will clear, and an orange precipitate of $\text{Fe}(\text{OH})_3(s)$ will form. The extent to which Fe^{3+} can exist in solution as a function of pH can be calculated from the solubility product, K_{so} . For $\text{Fe}(\text{OH})_3(s)$ the expression for K_{so} is given by:

$$K_{so} = [\text{Fe}^{3+}][\text{OH}^-]^3 = 10^{-39} \quad [2]$$

maximum Fe^{3+} conc at $[\text{OH}^-]$ indicated

One thus finds that the maximum concentration of Fe^{3+} in solution is controlled by pH, as detailed on the next slide.



Note that we need $[\text{OH}^-]$ in expression 2, which is obtained from the pH from equation 3.

$$\text{pK}_w = \text{pH} + \text{pOH} = 14 \quad [3]$$

Thus, if the pH is 2, then $\text{pOH} = 12$, and so on. pOH is related to $[\text{OH}^-]$ in the same way as pH is related to $[\text{H}^+]$.

$$\text{pH} = -\log [\text{H}^+] \quad [4]$$

$$\text{pOH} = -\log [\text{OH}^-] \quad [5]$$

So, to calculate the maximum concentration of $[\text{Fe}^{3+}]$ at pH 6.4, we use eqs. [3] to [5] to calculate that at pH 6.4, $\text{pOH} = 7.6$, so that $[\text{OH}^-] = 10^{-7.6} \text{ M}$. This is then used in equation [2] to calculate that $[\text{Fe}^{3+}]$ is given by:

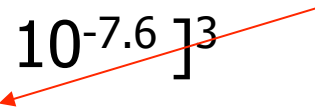


Problem. What is the maximum $[\text{Fe}^{3+}]$ at pH 6.4?

From the previous page, at pH 6.4 we have $[\text{OH}^-] = 10^{-7.6} \text{ M}$. Thus, putting $[\text{OH}^-] = 10^{-7.6} \text{ M}$ into equation 2, we get:

$$10^{-39} = [\text{Fe}^{3+}] \times [10^{-7.6}]^3$$

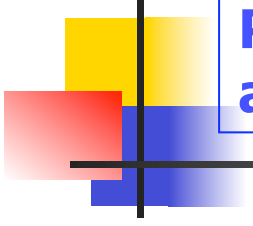
$= 3 \times -7.6$



$$[\text{Fe}^{3+}] = 10^{-39} / 10^{-22.8} = 10^{-16} \text{ M}$$

Note that for a metal ion M^{n+} of valence n that forms a solid hydroxide precipitate $\text{M}(\text{OH})_n$, the equation has the $[\text{OH}^-]$ raised to the power n . For example:





Problem: What is the maximum concentration of $[\text{Th}^{4+}]$ in aqueous solution at pH 4.2? ($\log K_{s0} = -50.7$)

At pH 4.2 $\text{pOH} = 14 - 4.2 = 9.8$.

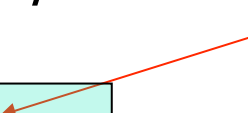
Thus, $[\text{OH}^-] = 10^{-9.8} \text{ M}$, so we have:

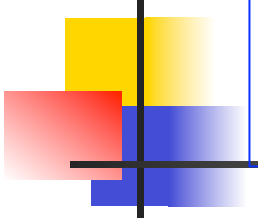
$$10^{-50.7} = [\text{Th}^{4+}] [10^{-9.8}]^4$$

$$10^{-50.7} = [\text{Th}^{4+}] \times 10^{-39.2}$$

$$[\text{Th}^{4+}] = 10^{-50.7} / 10^{-39.2}$$

$$= 10^{-11.5} \text{ M}$$

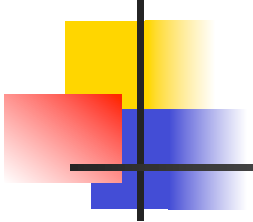
$$= -50.7 - (-39.2)$$




Factors that control the solubility of metal hydroxides.

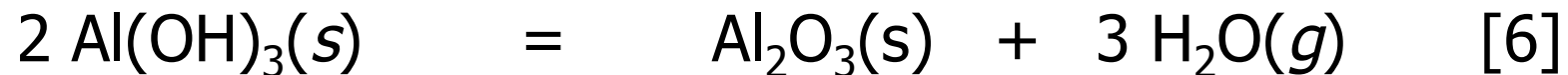
It is found that K_{so} is, like pK_a for aqua ions, a function of metal ion size, charge and electronegativity. Thus, Fe^{3+} is a small ion of fairly high charge, and not-too-low electronegativity, and so forms a hydroxide of low solubility. Thus, the hydroxide of Na^+ , which is $NaOH$, is highly soluble in water, while at the other extreme, $Pu(OH)_4(s)$ is of very low solubility ($K_{so} = 10^{-62.5}$). The latter fact is fortunate, because the highly radioactive $Pu(IV)$ is not readily transported in water, since it exists as a precipitated hydroxide. Examples of the effect of charge on solubility of hydroxides are:

	Ag^+	Cd^{2+}	La^{3+}	Th^{4+}
$\log K_{so}:$	-7.4	-14.1	-20.3	-50.7



Metal oxides and hydroxides.

Metal oxides can be regarded simply as dehydrated hydroxides. Metal hydroxides can usually be heated to give the oxides, although sometimes very high temperatures are required:



The formation of ceramics involves such firing of hydrated metal salts in a kiln, with waters of hydration being driven off. The oxides tend to be less soluble than the freshly precipitated hydroxides, and on standing many hydroxides lose water, and 'age'. Thus, aged precipitates of hydroxides can be much less soluble than freshly precipitated hydroxides. Fresh 'CaO' is quite water soluble, but old samples can be highly insoluble.

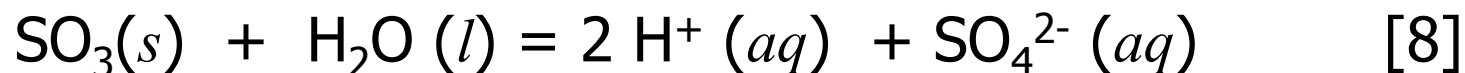


Amphoteric behavior.

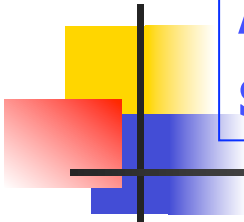
When one looks at the periodic table, one finds that at the very left, metal oxides are basic. That means that if they are dissolved in water, they give basic solutions:



On the right hand side, metal oxides dissolve to give acidic solutions, as with sulfur trioxide:



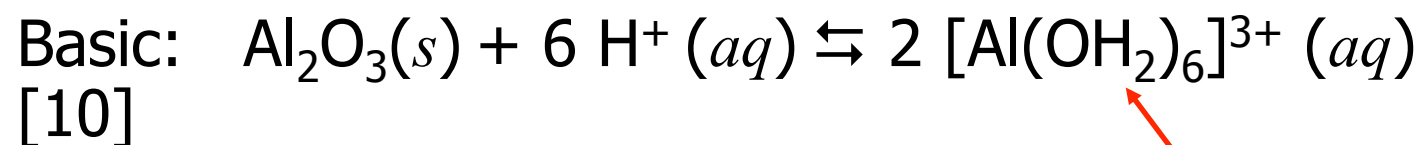
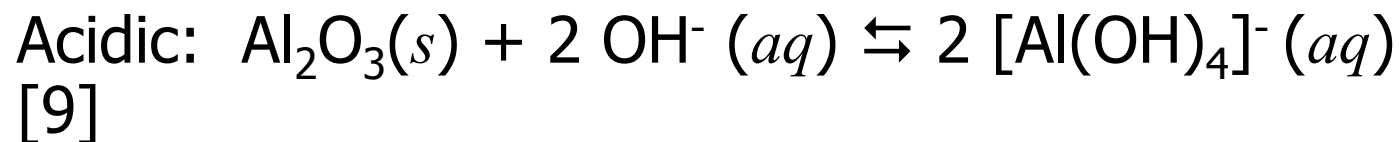
There is a transitional area where the metals can display both basic and acidic behavior. This is called *amphoteric* behavior.



Amphoteric behavior of Al(III) in aqueous solution:

Al(III) can display both acidic properties and basic properties:

tetrahydroxy aluminate anion

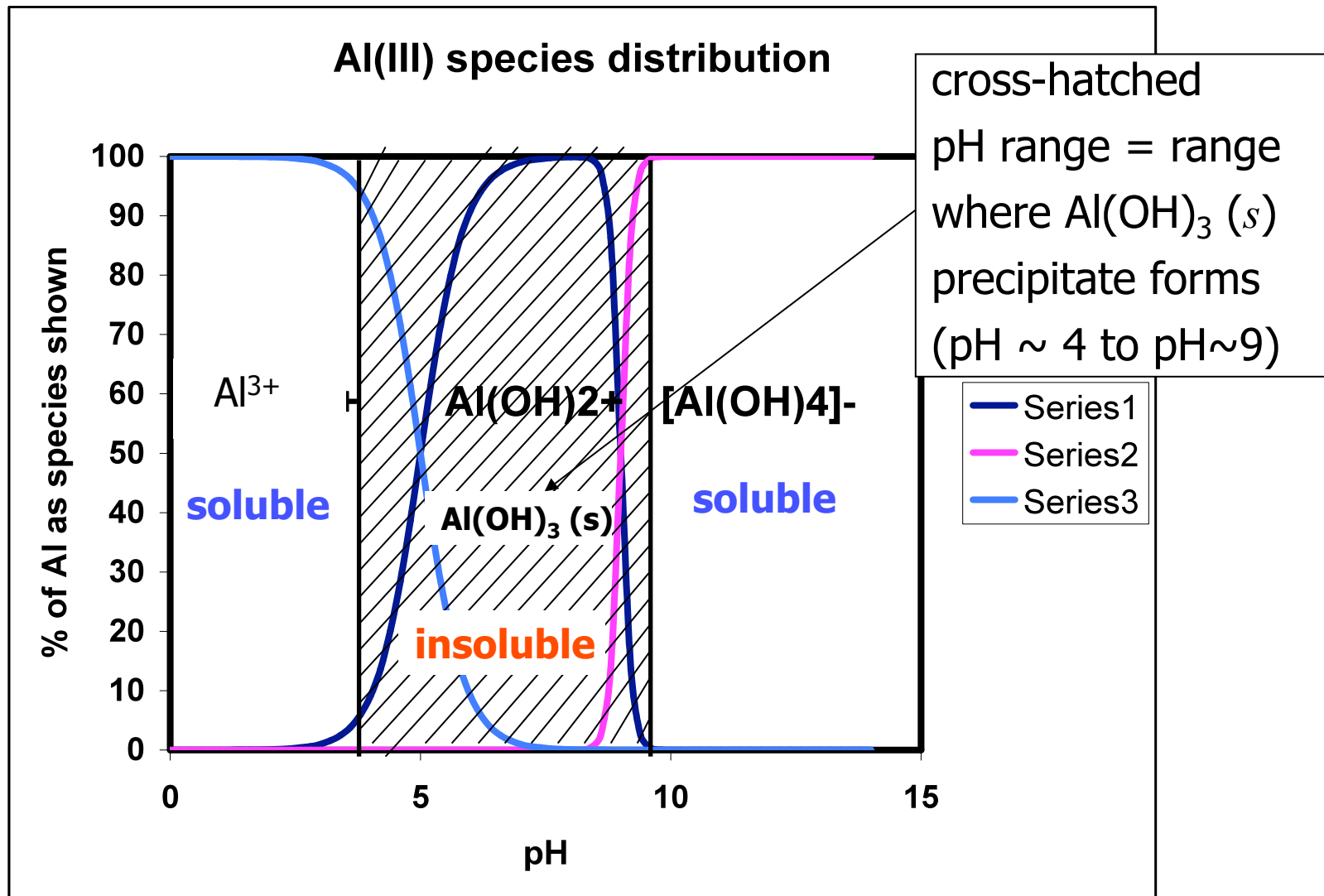


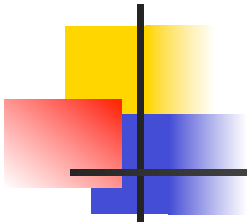
hexaaqua aluminum(III) cation



At high pH Al_2O_3 is acidic, while at low pH it is basic. The range of existence of the species $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$, and $[\text{Al}(\text{OH})_4]^-$ is shown in the species distribution diagram below:

Species distribution diagram for Al(III) in aqueous solution:





Amphoteric metal ions in the periodic table:

Metal ions that are amphoteric in the periodic table are highlighted in red below:

Zone of amphoteric metal ions

Be(II)	B(III)	C	N	O	F
Mg(II)	Al(III)	Si	P	S	Cl
Zn(II)	Ga(III)	Ge	As	Se	
	Br				
Cd(II)	In(III)	Sn (II)	Sb	Te	I
Hg(II)	Tl(III)	Pb(II)	Bi(III)	Po	

The species formed at high pH are, for example, the tetrahedral ions $[\text{Be}(\text{OH})_4]^{2-}$, $[\text{Zn}(\text{OH})_4]^{2-}$, $[\text{Al}(\text{OH})_4]^-$, $[\text{Ga}(\text{OH})_4]^-$, and $[\text{In}(\text{OH})_4]^-$.

Hard and Soft Acids and Bases.

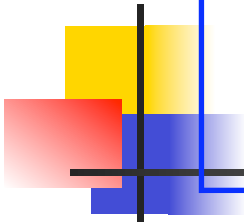
1 H														
3 Li	4 Be													
11 Na	12 Mg											13 Al	14 Si	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi
87 Fr	88 Ra	89 Ac												



hard soft intermediate

57 La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
----------	----	----	----	----	----	----	----	----	----	----	----	----	----	----

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk			
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Hard and Soft Acids and Bases.

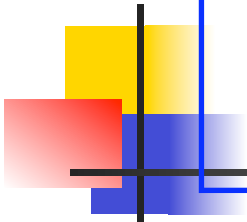
Pearson's Principle of Hard and Soft Acids and Bases (HSAB) can be stated as follows:

Hard Acids prefer to bond with Hard Bases, and Soft Acids prefer to bond with Soft Bases.

This can be illustrated by the formation constants ($\log K_1$) for a hard metal ion, a soft metal ion, and an intermediate metal ion, with the halide ions in Table 1:

Table 1. Formation constants with halide ions for a representative hard, soft and intermediate metal ion .

	hard ←			→ soft	
Log K_1	F ⁻	Cl ⁻	Br ⁻	I ⁻	classification
soft					
Ag ⁺	0.4	3.3	4.7	6.6	soft-soft interaction ↙
Pb ²⁺	1.3	0.9	1.1	1.3	
intermediate					
Fe ³⁺	6.0	1.4	0.5	-	hard
	↖ hard-hard interaction				



Hard and Soft Acids and Bases.

What one sees in Table 1 is that the soft Ag^+ ion strongly prefers the heavier halide ions Cl^- , Br^- , and I^- to the F^- ion, while the hard Fe^{3+} ion prefers the lighter F^- ion to the heavier halide ions. The intermediate Pb^{2+} ion shows no strong preferences either way. The distribution of hardness/softness of ligand donor atoms in the periodic Table is as follows:

Distribution of Hard and Soft Bases by donor atom in the periodic Table:

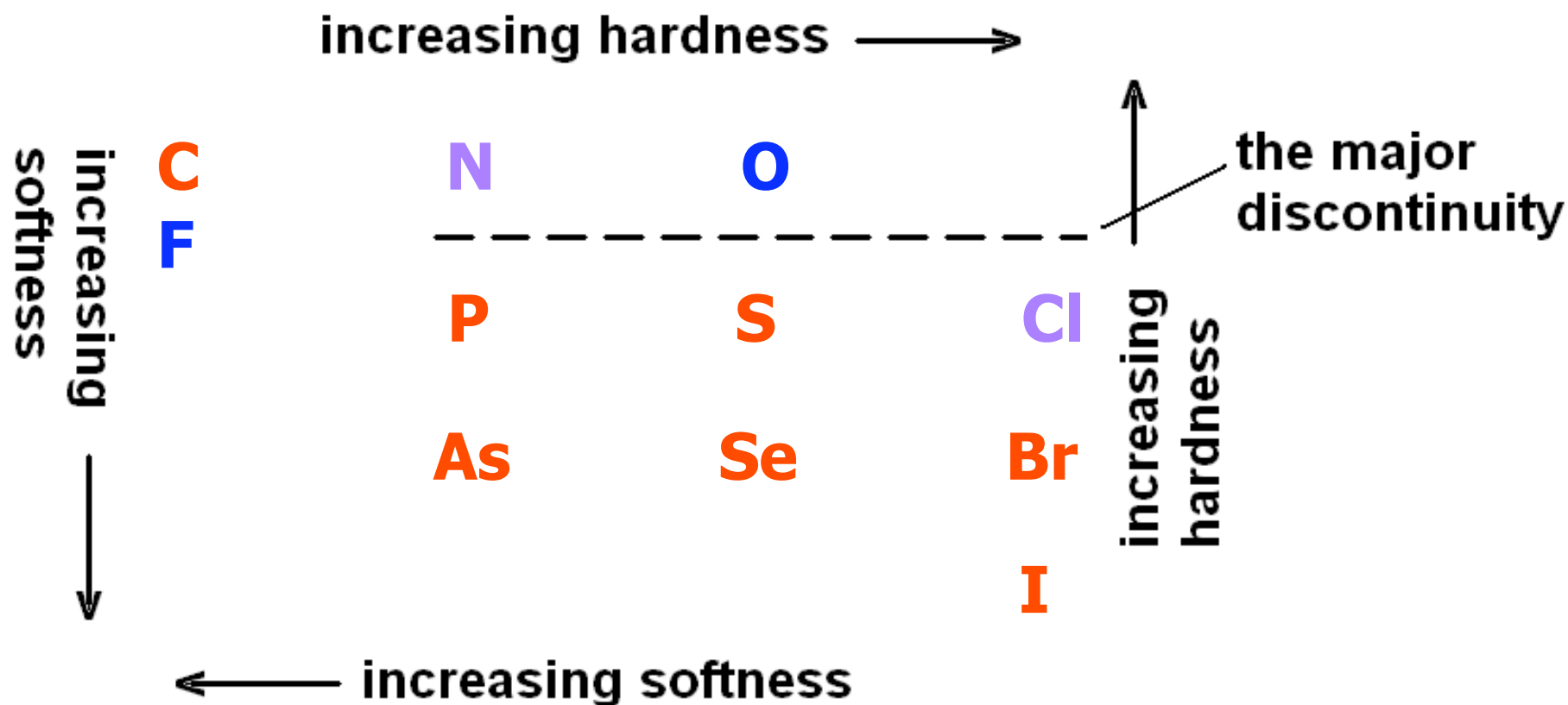
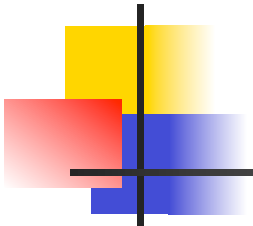


Figure 2. Distribution of hardness and softness for potential donor atoms for ligands in the Periodic Table.



Distribution of Hard and Soft Bases by donor atom in the Periodic Table.

The hardness of ligands tends to show, as seen in Figure 2, a discontinuity between the lightest member of each group, and the heavier members. Thus, one finds that the metal ion affinities of NH_3 are very different from metal ion affinities for phosphines such as PPh_3 (Ph = phenyl), but that the complexes of PPh_3 are very similar to those of AsPh_3 . A selection of ligands classified according to HSAB ideas are:



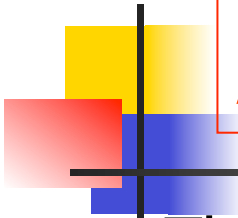
Hard and Soft Bases.

HARD: $\underline{\text{H}_2\text{O}}$, $\underline{\text{OH}^-}$, $\text{CH}_3\underline{\text{COO}^-}$, $\underline{\text{F}^-}$, $\underline{\text{NH}_3}$,
oxalate ($^-\underline{\text{OOC}}-\underline{\text{COO}^-}$), en ($\underline{\text{NH}_2}\text{CH}_2\text{CH}_2\underline{\text{NH}_2}$).

SOFT: $\underline{\text{Br}^-}$, $\underline{\text{I}^-}$, $\underline{\text{SH}^-}$, $\text{CH}_3\underline{\text{S}^-}$, $(\text{CH}_3)_2\underline{\text{S}}$,
 $\underline{\text{S}}=\text{C}(\text{NH}_2)_2$ (thiourea), $\underline{\text{P}}(\text{CH}_3)_3$, $\underline{\text{P}}\text{Ph}_3$,
 $\underline{\text{As}}(\text{CH}_3)_3$, $\underline{\text{CN}^-}$, $^-\underline{\text{S}}-\text{C}\equiv\text{N}$ (thiocyanate, S-
bound)

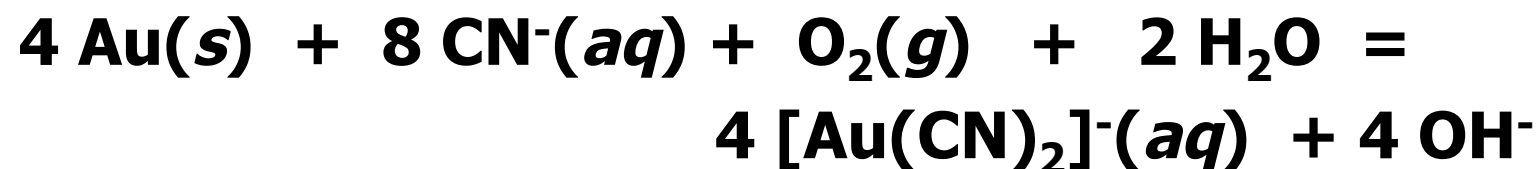
INTERMEDIATE: $\text{C}_6\text{H}_5\underline{\text{N}}$ (pyridine), $\underline{\text{N}_3^-}$
(azide), $^-\underline{\text{N}}=\text{C}=\text{S}$ (thiocyanate, N-bound),
 $\underline{\text{Cl}^-}$

(donor atoms underlined)

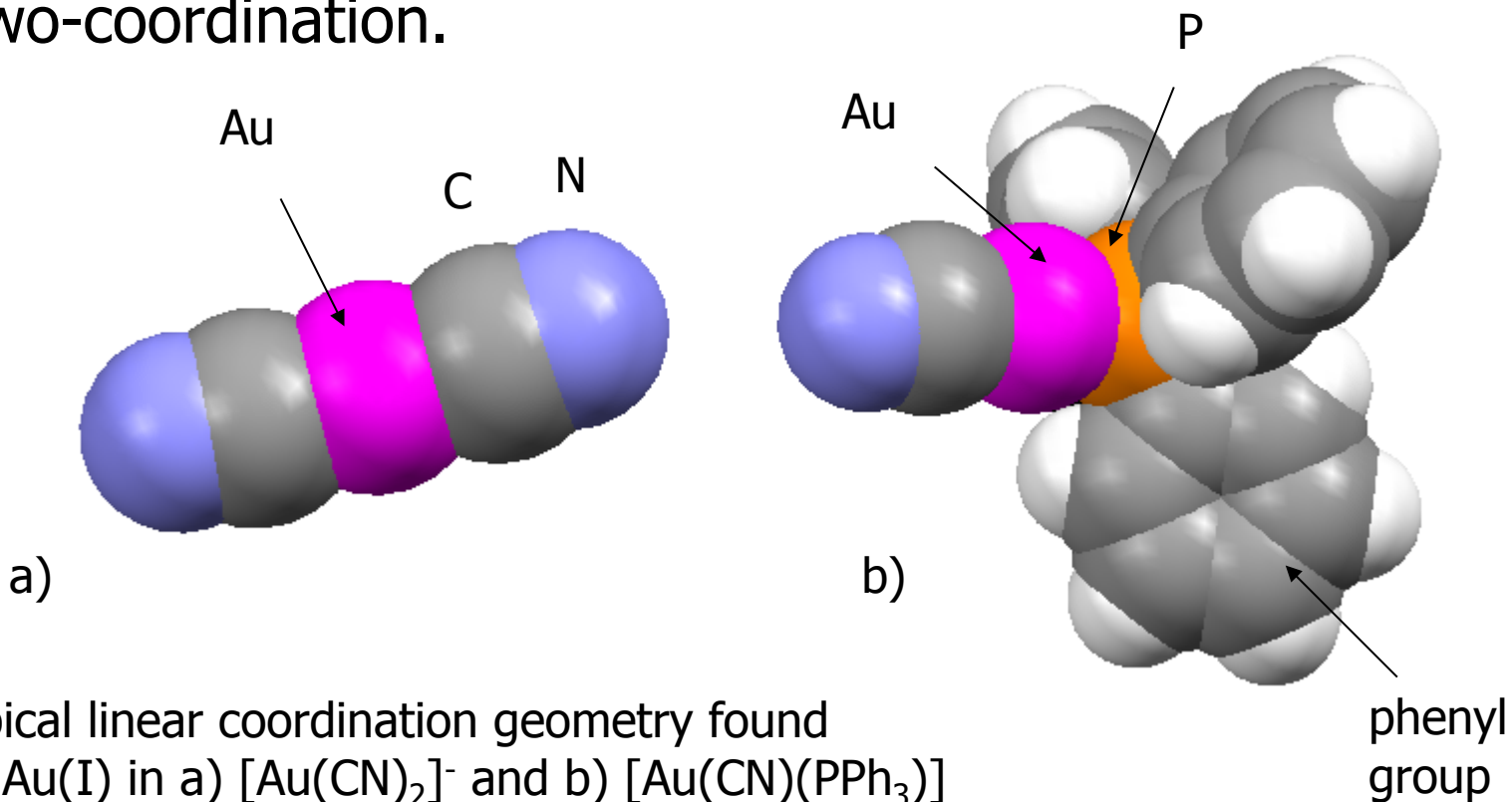


A very soft metal ion, Au(I):

The softest metal ion is the $\text{Au}^+(\text{aq})$ ion. It is so soft that the compounds AuF and Au_2O are unknown. It forms stable compounds with soft ligands such as PPh_3 and CN^- . The affinity for CN^- is so high that it is recovered in mining operations by grinding up the ore and then suspending it in a dilute solution of CN^- , which dissolves the Au on bubbling air through the solution:



The aurocyanide ion is linear, with two-coordinate Au(I). This is typical for Au(I), that it prefers linear two-coordination. This coordination geometry is seen in other complexes of Au(I), such as $[\text{AuPPh}_3\text{CN}]$, for example. Neighboring metal ions such as Ag(I) and Hg(II) are also very soft, and show the same unusual preference for two-coordination.





A very hard metal ion, Al(III):

An example of a very hard metal ion is Al(III). It has a high $\log K_1$ with F^- of 7.0, and a reasonably high $\log K_1(OH^-)$ of 9.0. It has virtually no affinity in solution for heavier halides such as Cl^- . Its solution chemistry is dominated by its affinity for F^- and for ligands with negative O-donors.

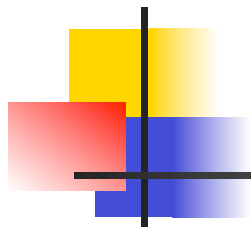
One can rationalize HSAB in terms of the idea that **soft-soft interactions are more covalent**, while **hard-hard interactions are ionic**. The covalence of the soft metal ions relates to their higher electronegativity, which in turns depends on relativistic effects.



What one needs to be able to comment on is sets of formation constants such as the following:

Metal ion:	Ag⁺	Ga³⁺	Pb²⁺
log K₁(OH⁻):	2.0	11.3	6.0
log K₁(SH⁻):	11.0	8.0	6.0

What is obvious here is that the soft Ag⁺ ion prefers the soft SH⁻ ligand to the hard OH⁻ ligand, whereas for the hard Ga³⁺ ion the opposite is true. The intermediate Pb²⁺ ion has no strong preference.



Another set of examples is given by:

Metal ion:	Ag⁺	H⁺
Log K_1 (NH₃):	3.3	9.2
Log K_1 (PPh₃):	8.2	0.6

Again, the soft Ag⁺ ion prefers the soft phosphine ligand, while the hard H⁺ prefers the hard N-donor.

Thiocyanate, an ambidentate ligand:

Thiocyanate (SCN^-) is a particularly interesting ligand. It is ambidentate, and can bind to metal ions either through the S or the N. Obviously, it prefers to bind to soft metal ions through the S, and to hard metal ions through the N. This can be seen in the structures of $[\text{Au}(\text{SCN})_2]^-$ and $[\text{Fe}(\text{NCS})_6]^{3-}$ in Figure 3 below:

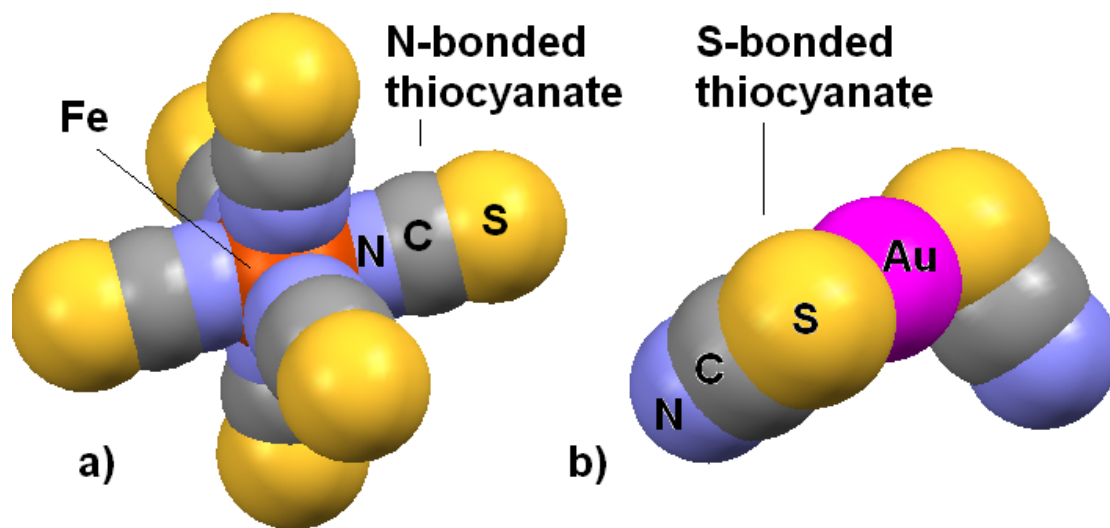


Figure 3. Thiocyanate Complexes showing a) N-bonding in the $[\text{Fe}(\text{NCS})_6]^{3-}$ complex with the hard $\text{Fe}(\text{III})$ ion, and b) S-bonding in the $[\text{Au}(\text{SCN})_2]^-$ complex with the soft $\text{Au}(\text{I})$ ion

Cu(I) and Cu(II) with thiocyanate:

In general, intermediate metal ions also tend to bond to thiocyanate through its N-donors. A point of particular interest is that Cu(II) is intermediate, but Cu(I) is soft. Thus, as seen in Figure 4, $[\text{Cu}(\text{NCS})_4]^{2-}$ with the intermediate Cu(II) has N-bonded thiocyanates, but in $[\text{Cu}(\text{SCN})_3]^{2-}$, with the soft Cu(I), S-bonded thiocyanates are present.

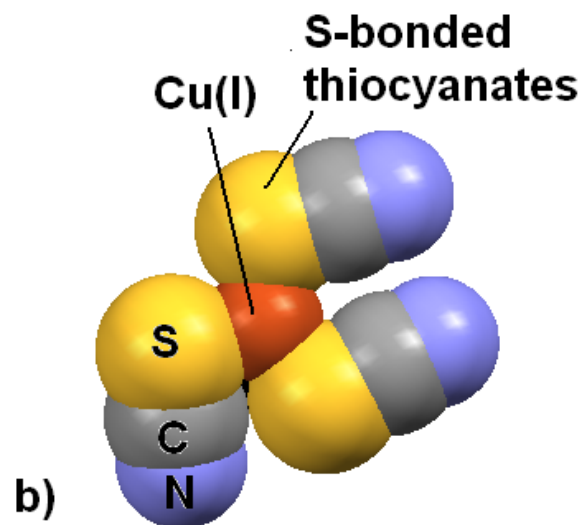
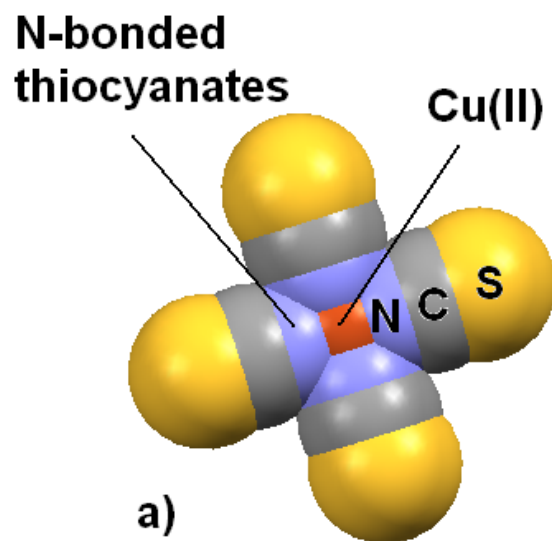


Figure 4. Thiocyanate complexes of the intermediate Cu(II) ion and soft Cu(I) ion. At a) the thiocyanates are N-bonded in $[\text{Cu}(\text{NCS})_4]^{2-}$ with the intermediate Cu(II), but at b) the thiocyanates in $[\text{Cu}(\text{SCN})_3]^{2-}$, with the soft Cu(I), are S-bonded.