Hard and Soft Acids and Bases (HSAB)

The affinity that metal ions have for ligands is controlled by size, charge and electronegativity. This can be refined further by noting that for some metal ions, their chemistry is dominated by size and charge, while for others it is dominated by their electronegativity. These two categories of metal ions have been termed by Pearson as hard metal ions and soft metal ions. Their distribution in the periodic table is as follows:

![Hard, soft, intermediate Lewis Acids in the Periodic Table](image)

**Figure 1.** Table showing distribution of hard, soft, and intermediate Lewis Acids in the Periodic Table, largely after Pearson.

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.* The concept assigns ions, molecules and atoms with a 'hard' character as acids, and those with a 'soft' character as bases. Hard ions show a high charge density (high ratio of charge to radius) and are not easily polarized, while soft ions show a low charge density (low ratio of charge to radius) and are therefore easily polarized.

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.

<table>
<thead>
<tr>
<th>Log $K_1$</th>
<th>F⁻</th>
<th>Cl⁻</th>
<th>Br⁻</th>
<th>I⁻</th>
<th>classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺</td>
<td>0.4</td>
<td>3.3</td>
<td>4.7</td>
<td>6.6</td>
<td>soft</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>1.3</td>
<td>0.9</td>
<td>1.1</td>
<td>1.3</td>
<td>intermediate</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>6.0</td>
<td>1.4</td>
<td>0.5</td>
<td>-</td>
<td>hard</td>
</tr>
</tbody>
</table>
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:

![Figure 2. Distribution of hardness and softness for potential donor atoms for ligands in the Periodic Table. The diagram shows that hardness increases toward F\(^{-}\), and softness increases away from F\(^{-}\). However, this is not a smooth transition. There is, as shown, a major discontinuity between the lighter members of each group, namely, F, O, and N, and their heavier congeners. Thus, Cl\(^{-}\), Br\(^{-}\), and I\(^{-}\) are far more like each other, and far different from F\(^{-}\), in their bonding preferences, as can be seen in Table 1.](image)

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 acids**: H\(^+\); Na\(^+\); K\(^+\); Cr\(^{3+}\); Cr\(^{6+}\); BF\(_3\); Mn\(^{2+}\); Al\(^{3+}\); Co\(^{3+}\); Ga\(^{3+}\); Fe\(^{3+}\); Mg\(^{2+}\); Ca\(^{2+}\); (Cu\(^{2+}\))
- **Soft acids**: Pt\(^{2+}\); Pt\(^{4+}\); Pb\(^{2+}\); Au\(^{+}\); Hg\(^{2+}\); Hg\(^{2+}\); Cd\(^{2+}\); Cu\(^+\); Pb\(^{2+}\); BH\(_3\); Ag\(^{+}\); Ti\(^+\)
- **Hard bases**: H\(_2\)O; OH\(^-\); F\(^-\); Cl\(^-\); NH\(_3\); R\(_3\)N; oxalate (\(^{-}\)OOC-COO\(^-\)); CH\(_3\)COO\(^-\); CO\(_3^{2-}\); N\(_2\)H\(_4\); PO\(_4^{3-}\)
- **Soft bases**: SCN\(^-\) (S-bound); S=C(NH\(_2\))\(_2\) (thiourea), R\(_2\)S; SH\(^-\); P(CH\(_3\))(\(_3\))\(_3\); PPH\(_3\); As(CH\(_3\))(\(_3\))\(_3\); CN\(^-\); Br\(^-\); I\(^-\)
- **Intermediate**: C\(_6\)H\(_5\)N (pyridine), N\(_3\)^(-); N=C=S N-bound), Cl\(^-\)

The softest metal ion is the Au\(^{+}\) (aq) ion. It is so soft that the compounds AuF and Au\(_2\)O 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:

\[
4 \text{Au}(s) + 8 \text{CN}^-(aq) + O_2(g) + 2 \text{H}_2\text{O} = 4 \left[\text{Au(CN)}_2\right]^-(aq) + 4 \text{OH}^- \quad [1]
\]
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 [AuPPh₃Cl], for example. Neighboring metal ions such as Ag(I) and Hg(II) are also very soft, and show the unusual preference for two-coordination.

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

This is also documented by the following sets of formation constants:

<table>
<thead>
<tr>
<th>Metal ion:</th>
<th>Ag⁺</th>
<th>Ga³⁺</th>
<th>Pb²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log $K_1(\text{OH}^-)$:</td>
<td>2.0</td>
<td>11.3</td>
<td>6.0</td>
</tr>
<tr>
<td>Log $K_1(\text{SH}^-)$:</td>
<td>11.0</td>
<td>8.0</td>
<td>6.0</td>
</tr>
</tbody>
</table>

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:

<table>
<thead>
<tr>
<th>Metal ion:</th>
<th>Ag⁺</th>
<th>H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log $K_1(\text{NH}_3)$:</td>
<td>3.3</td>
<td>9.2</td>
</tr>
<tr>
<td>Log $K_1(\text{PPh}_3)$:</td>
<td>8.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>

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

Thiocyanate ($\text{SCN}^-$) is a particularly interesting ligand. It can bind to metal ions either through the S or the N atom. Obviously, it prefers to bind to soft metal ions through S, and to hard metal ions through N. This can be seen in the structures of [Au(SCN)$_2]$ and [Fe(NCS)$_6]$� in Figure 3 below.
Figure 3. Thiocyanate complexes showing a) N-bonding in the [Fe(NCS)_6]^{3-} complex with the hard Fe(III) ion, and b) S-bonding in the [Au(SCN)_2]^{-} complex with the soft Au(I) ion (CSD: AREKOX).

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, [Cu(NCS)_4]^{2-} with the intermediate Cu(II) forms N-bonded thiocyanates, but in [Cu(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. Note that in a) the thiocyanates are N-bonded in [Cu(NCS)_4]^{2-} with the intermediate Cu(II), but in b) the thiocyanates in [Cu(SCN)_3]^{2-}, with the soft Cu(I), are S-bonded (CSD: PIVZOJ).