Color, Transition Metal Complexes, Thermodynamic and Kinetic Stability

What determines color? Absorption of some portion of the electromagnetic spectrum in the visible region. The color observed when light is passed through a transparent medium or when reflected from a surface is the complement to the color of the radiation actually absorbed.

What is necessary for absorption of electromagnetic radiation in the visible region, and thus the appearance of color? Absorption of light is absorption of energy; therefore, since light energies are quantized there must be an energy change equal to the energy of the wavelengths absorbed. Usually this involves an electronic transition between the ground and an excited state.

Transition metal compounds are frequently colored and the color of a particular metal ion will depend upon its environment. Thus Ni(ClO$_4$)$_2$·6H$_2$O, which is more correctly as [Ni(OH)$_2$]$_6$(ClO$_4$)$_2$ is green, whereas [Ni(en)$_3$](ClO$_4$)$_2$, where en = H$_2$NCH$_2$CH$_2$NH$_2$ (called ethylenediamine) and each nitrogen atom is bonded to the nickel ion is purple. The structures of these ions are shown below.

![Structure of Ni(OH)$_2$]$_6$(ClO$_4$)$_2$](image1)

![Structure of Ni(en)$_3$](image2)

Solid [Co(OH)$_2$]$_6$Cl$_2$ is pink and maintains this color when dissolved in water. However, when this salt is dissolved in ethanol (ethyl alcohol) the color is a very intense “cobalt” blue. The blue color is due to the formation of CoCl$_4^{2-}$ ion. Simple consideration of stoichiometry indicates that a maximum of 50% of the cobalt can be present in this form. The rest is in the form of [Co(OH)$_2$]$_6$(HOCH$_2$CH$_2$)$_{6-x}$[CoCl$_4^{2-}$]. The color of the CoCl$_4^{2-}$ ion is much more intense than that of the six-coordinate species so that the presence of the latter is not detectable to the eye.

Transition metal complexes may be very stable, or very reactive. The stabilities of transition metal complexes may be thermodynamic or kinetic in origin. For example we saw that the reaction [Ni(OH)$_2$]$_6^{2+}$ + 3 en → [Ni(en)$_3$]$_2^{2+}$ + 6 H$_2$O occurred immediately upon addition of the ethylenediamine. The formation of the violet product is a result of the thermodynamic stability of the products compared to the reactants. That the reaction was rapid is a result of a low energy barrier to the reaction, or a kinetic instability for [Ni(OH)$_2$]$_6^{2+}$.

Addition of acid to [Ni(en)$_3$]$_2^{2+}$ resulted in immediate disappearance of the purple color of the latter species and the reformation of the green color of [Ni(OH)$_2$]$_6^{2+}$. The stoichiometry of the reaction is [Ni(en)$_3$]$_2^{2+}$ + 6 H$_3$O$^+$ → [Ni(OH)$_2$]$_6^{2+}$ + 3 [H$_2$NCH$_2$CH$_2$NH$_2$]$_3^{3+}$. The fact that it occurs is a result of greater thermodynamic stability.
of the products compared to the reactants. That the reaction was instantaneous is a result of a low energy barrier or a kinetic instability of the starting complex.

The thermodynamics of reaction of \([\text{Co(en)}_3]^{3+}\), which has the same structure as the corresponding Ni(II) complex ion, with acid are also highly favorable yet this reaction does not occur at room temperature. This is a result of the properties of the Co(III)-nitrogen interaction which result in a high energy barrier for reaction, or a high kinetic stability.

The structure of the molecule(s) bonded to a metal ion can affect the reactivity (kinetic stability) of the ion. For example the nickel(II) complex shown below is as unreactive toward acid as the \([\text{Co(en)}_3]^{3+}\) ion although thermodynamically protonation of the amine groups and formation of \([\text{Ni(OH}_2)_6]^{2+}\) is thermodynamically favorable.

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\begin{array}{c}
\text{H} \\
\text{Ni} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
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That there was a significant enhancement of the color of the solution of this complex when acid was added, rather than the bleaching that should have occurred upon dilution is an interesting point. This is due to position of the following equilibrium being shifted markedly to the right. The four-coordinate species is yellow orange (absorbs at 450 nm) whereas the six-coordinate species with both amine and water bonded to the metal ion is a much less intense blue-violet color. For reasons that are not totally clear, a change in ionic strength results in a shift from six-coordinate to four-coordinate compound.