



The Colours of Complexes

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ABSTRACT:

The d-orbitals of a free transition metal atom or ion degenerate (all have the same energy.) However, when transition metals form coordination complexes, the d-orbitals of the metal interact with the electron cloud of the ligands in such a way. have a conversation. that the d-orbitals become non-degenerative (not all have the same energy.) The way in which the orbitals are split into different energy levels depends on the geometry of the complex. Crystal field theory can be used to predict the energies of different d-orbitals, and how a transition metal's d-electrons are distributed among them. When the d-level is not completely filled, it is possible to promote an electron from a lower energy d-orbital to a higher energy d-orbital by the absorption of a photon of electromagnetic radiation with the appropriate energy. Electromagnetic radiations in the visible region of the spectrum often possess the appropriate energy for such transitions.

INTRODUCTION:

The human eye perceives a mixture of all the colors present in sunlight as white light. Complementary colors, which are located across from each other on a color wheel, are also used in color vision. The eye perceives a mixture of two complementary colors in the appropriate proportions as white light. Similarly, when a color is missing from white light, the eye sees its complement. For example, when red photons are absorbed by white light, the eye sees green. When violet photons are removed from white light, the eye appears lemon yellow.

The blue color of the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion results because this ion absorbs orange and red light, leaving the complementary colors of blue and green. If white light (for example ordinary sunlight) passes through a $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ solution, some of the wavelengths in the light are absorbed by the solution. In solution $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ions absorb light in the red region of the spectrum. The light that passes through the solution to the other side will have all the colors



except red. We see this mixture of wavelengths as light blue (cyan). This diagram gives an idea of what happens if you pass white light through $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ solution.

The Color Wheel

The visible part of the electromagnetic spectrum consists of light of wavelength 380–750 nm. The color wheel below gives information about the wavelength and complementary color of different colors. For example: if red light is absorbed, the compound appears green; If violet light is absorbed, the compound appears yellow.



It's not easy to figure out which color you'll see if you try to do this by imagining "mixing" the rest of the colors. You might not have thought that all colors except some would look cyan, for example. Sometimes what you actually see is quite unexpected. Mixing different wavelengths of light doesn't give you the same results as mixing paint or other pigments. However, you can sometimes use the idea of complementary colors to get some idea of the color you'll see.

Remember that the color we see when we look at an object or compound is due to the light that is transmitted or reflected, not the light that is absorbed, and that reflected or transmitted light is due to the absorbed light. Complementary in color. Thus a green compound absorbs light in the red part of the visible spectrum and vice versa, as indicated by the complementary color wheel.

The striking colors displayed by transition-metal complexes are due to the excitation of an electron from a low-energy d orbital to a high-energy d orbital, called the d–d transition. For a photon to effect such a transition, its energy must be equal to the energy difference between the two d orbitals, which depends on the magnitude of Δ_o .

Color Depends on Oxidation State



Small changes in the relative energy of the orbitals that are transitioning between electrons can cause a drastic change in the color of the absorbed light. Therefore, the colors of coordination compounds depend on many factors. Different aqueous metal ions can have different colors. In addition, different oxidation states of a metal can produce different colors.

Color Depends on Ligand Field

Specific ligands coordinated to the metal center also affect the color of the coordination complexes. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a compound depends on the magnitude of Δ_o , which depends on the composition of the compound. For example, the complex $[\text{Cr}(\text{NH}_3)_6]^{3+}$ has strong field ligands and relatively large Δ_o . As a result, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellowish hue. A related complex with a weak field ligand, the $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ion, absorbs low-energy photons corresponding to the yellow-green part of the visible spectrum, giving it a deep purple color. For example, the iron(II) complex $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4$ appears blue-green because the high-spin complex absorbs photons at red wavelengths. In contrast, the low-spin iron(II) complex $\text{K}_4[\text{Fe}(\text{CN})_6]$ appears pale yellow because it absorbs high-energy violet photons.

In general, strong-field ligands cause a large split in the energy of the d orbitals of the central metal atom (large Δ_{oct}). Transition metal coordination compounds with these ligands are yellow, orange or red because they absorb high-energy violet or blue light. On the other hand, coordination compounds of transition metals containing weak field ligands are often blue-green, blue or indigo because they absorb low-energy yellow, orange or red light.

A coordination compound of Cu ion has d^{10} configuration, and all e.g. orbitals are filled. To excite an electron to a higher level, such as a 4p orbital, photons with very high energies are necessary. This energy corresponds to very short wavelengths in the ultraviolet region of the spectrum. No visible light is absorbed, so the eye sees no change, and the compound appears white or colorless. For example, a solution containing $[\text{Cu}(\text{CN})_2]^-$ is colourless. On the other hand, in octahedral Cu^{2+} complexes such as $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ there is a vacancy, and electrons can be excited to this level. The wavelength (energy) of the absorbed light corresponds to the visible part of the spectrum, and Cu^{2+} complexes are almost always colored—blue, blue-green violet, or yellow. Although CFT successfully describes many properties of coordination complexes, molecular orbital explanations (beyond the introductory scope provided here) are needed to fully understand the behavior of coordination complexes.



Selection rules for electronic transitions

The Beer-Lambert Law

$$A = \log_{10}(I_0/I) = \epsilon cl$$

where ϵ is the molar extinction coefficient (in $\text{L cm}^{-1} \text{mole}^{-1}$), c is concentration in mole L^{-1} and l is the path length in cm. A is known as 'Absorbance' and it is dimensionless.

To interpret the absorption spectra of coordination complexes, it is necessary to know the selection rules governing electronic transitions. Any transition in violation of the selection rule is said to be 'forbidden', but we will see how some rules are 'more prohibited than others'. We will not follow the theoretical basis of the rules, but only outline simple tests for their application.

The Laporte Rule.

In a molecule or ion with a symmetry center, the transition between orbitals with the same symmetry is not allowed, for example from d to d . In other words, there must be a change in parity ($\Delta l = \pm 1$), i.e. the orbital quantum number must be different from 0. The forbidden transitions are $s \rightarrow s$, $d \rightarrow d$, $p \rightarrow p$ etc. Geometry influenced by this law includes octahedral and square-planar complexes. This rule does not apply to tetrahedral complexes because they do not have a center of symmetry.

The key element here is that there are mechanisms by which selection rules can be relaxed so that transitions can occur, even if at low intensity. The asymmetric vibrations of an octahedral complex can momentarily destroy its center of symmetry and allow transitions that would otherwise be Laporte prohibited. In cases where the rule applies, the colors of the complexes are usually relatively light. As an example, consider $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, which is a lighter blue color than $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

Spin Allowed - Spin Forbidden

Any transition for which $\Delta S \neq 0$ is strictly prohibited; That is, to be allowed, a transition must not involve any change in the spin state. Consider the case of the high spin d^5 complex $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$. Electronic transition is not only prohibited Laporte but spin is also prohibited. Absorptions with doubly forbidden transitions are extremely weak. It is then understood that dilute solutions of $\text{Mn}(\text{II})$ are colourless. which is dark blue.

Gems - A ruby is a pink to blood-red colored gemstone that contains trace amounts of chromium in the mineral corundum Al_2O_3 . In contrast, trace amounts of chromium within the $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ matrix give it an emerald green color. Now we can understand why



emeralds and rubies have such different colors, even though they both contain Cr^{3+} in an octahedral environment provided by six oxide ions. Although the chemical identities of the six ligands are the same in both cases, the Cr–O distances are different because the host lattice compositions are different (Al_2O_3 in ruby and $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ in emerald). In ruby, the Cr–O distance is relatively short due to the constraints of the host lattice, which enhances the d orbital–ligand interaction and makes Δ_o relatively large. As a result, rubies absorb green light and transmitted or reflected light is red, which gives the gemstone its distinctive color. In emerald, the Cr–O distance is longer due to the relatively large $[\text{Si}_6\text{O}_{18}]^{12-}$ silicate rings; This results in a reduction in the d orbital–ligand interaction and a smaller Δ_o . As a result, the emerald absorbs light of a longer wavelength (red), which gives the gem its characteristic green color. It is clear that the transition-metal ion environment, which is determined by the host lattice, dramatically affects the metal ion's spectroscopic properties.

Absorption spectrum of a ruby. The number and position of the peaks in the spectrum are determined by the electronic structure of the compound, which in this case depends on the identity, number and geometry of the metal and the surrounding ions. Crystal field theory can be used to predict the electronic structure and thus the absorption spectrum. If white light is shown on the gem, the absorption spectrum indicates which wavelengths of light have been removed. In this case, there are strong bands centered at 414 and 561 nm. These wavelengths correspond to blue and yellow-green light, respectively. For the most part, these colors are not present in the light reaching one's eyes. An alternative way of expressing this concept is to recognize that the spectrum of light reaching the eye is the product of the spectrum of incident light (white light) and the transmittance spectrum. For this ruby, the transmittance spectrum has a peak at 481 nm and a broad plateau at 620 nm. (Note that there is significant attenuation of light throughout the spectrum.) Thus only light reaches the eye with wavelengths near 481 nm (cyan) and wavelengths greater than 620 nm (red).

A similar analysis of the spectrum of the emerald is possible. The absorption spectrum shows strong bands at 438 and 606 nm, which remove blue and orange light, respectively. Light that is not absorbed is shown by the transmittance spectrum, which indicates that the dominant band of light reaching the eye is focused at 512 nm (green light), with smaller than the distant blue and red portions of the spectrum. contributions are made. This combination of wavelengths produces the dark green color.



CONCLUSION

When atoms or molecules absorb light at the appropriate frequency, their electrons are excited to higher-energy orbitals. For many main group atoms and molecules, the absorbed photons are in the ultraviolet range of the electromagnetic spectrum, which cannot be detected by the human eye. For coordination compounds, the energy difference between d orbitals often allows photons to be absorbed in the visible range.

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