# **Color of Transition Metal Complexes**

The variety of color among transition metal complexes has long fascinated the chemists. For example, aqueous solutions of  $[Fe(H_2O)_6]^{3+}$  are red,  $[Co(H_2O)_6]^{2+}$  are pink,  $[Ni(H_2O)_6]^{2+}$  are green,  $[Cu(H_2O)_6]^{2+}$  are blue and  $[Zn(H_2O)_6]^{2+}$  are colorless. Although the octahedral  $[Co(H_2O)_6]^{2+}$  are pink, those of tetrahedral  $[CoCl_4]^{2-}$  are blue. The green color of  $[Ni(H_2O)_6]^{2+}$  turns blue when ammonia is added to give  $[Ni(NH_3)_6]^{2+}$ . Many of these facts can be rationalized from CFT.



# Why we see Color?

When a sample absorbs light, what we see is the sum of the remaining colors that strikes our eyes. If a sample absorbs all wavelength of visible light, none reaches our eyes from that sample, and then the sample appears black. If the sample absorbs no visible light, it is white or colorless. When the sample absorbs a photon of visible light, it is its complementary color we actually see. For example, if the sample absorbed orange color, it would appear blue; blue and orange are said to be complementary colors.

### The Color Wheel

the

also

The visible part of the electromagnetic spectrum contains light of wavelength 380-750 nm. The color wheel below gives information on the wavelength of different color and

color. For e	xample	: If red
Re	d Or	ange
Violet	$\left \right $	Yellow
В	Je Gi	reen

complementary

light is absorbed, the complex appears green; If

Colour of light absorbed	Approx. $\lambda$ ranges / nm	Colour of light transmitted
Red	700-620	Green
Orange	620-580	Blue
Yellow	580-560	Violet
Green	560-490	Red
Blue	490-430	Orange
Violet	430-380	Yellow

purple light is absorbed, the complex appears yellow.

#### **Color of Coordination Complexes**

The color of coordination complexes arises from electronic transitions between levels whose spacing corresponds to the wavelengths available in the visible light. In complexes, these transitions are frequently referred to as d-d transitions because they involve the orbitals that are mainly d in character (for examples:  $t_{2g}$  and  $e_g$  for the octahedral complexes and e and  $t_2$  for the tetrahedral complexes). Obviously, the colors exhibited are intimately related to the magnitude of the spacing between these levels. Since this spacing depends on factors such as the geometry of the complex, the nature of the ligands, and the oxidation state of the central metal atom, variation on colors can often be explained by looking carefully at the complexes concerned. Below are a few examples to illustrate this point.



• The variation in the color of the Cr(III) complexes can be explained following similar argument



We observe the appearance of a shoulder in the case of  $[Ti(H_2O)_6]^{3+}$ . Perfectly octahedral  $[Ti(H_2O)_6]^{3+}$  should give only one d-d Transition. However, distortion occurs to eliminate the degeneracy of the system. If a complex distorts from regular octahedral geometry, the  $t_{2g}$  and  $e_g$  levels are split, the consequence of which is the appearance of a shoulder as shown in the figure right.



- Complexes that contain metal ions of  $d^{10}$  electron configuration are usually colorless. Examples are  $[Cu(PPh_3)_4]^+$  and  $[Zn(H_2O)_6]^{2+}$ . One would expect a metal complex with no d-eletron to be colorless as well. However, a few of such complexes are strongly colored, for example,  $MnO_4^-$  or  $[Cr_2O_7]^{2-}$ . The origin of the color in these complexes is not the d-d transitions, rather due to 'charge transfer' that we will briefly discuss later.
- Multi-electron systems exhibit multiple transitions and the assignment of absorption bands is not straightforward. The complexity arises due to interelectron repulsions that we will not discuss in this course but will take a simpler approach to understand the color of coordination complexes.

#### Selection rules for electronic transitions

The Beer-Lambert Law

$$A = log_{10}(I_o/I) = \varepsilon cl$$

where  $\varepsilon$  is the molar extinction coefficient (in L cm<sup>-1</sup> mole<sup>-1</sup>), c is concentration in mole L<sup>-1</sup> and l is the path length in cm. A is known as 'Absorbance' and it is dimensionless.

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

The Laporte Rule. In a molecule or ion possessing a centre of symmetry, transitions are not allowed between orbitals of the same parity, for example d to d. In other words, there must be change in parity ( $\Delta l=\pm 1$ ), i.e. the orbital quantum number should differ by 1. The forbidden transitions are s  $\rightarrow$  s, d  $\rightarrow$  d, p  $\rightarrow$  f. etc. The geometries affected by this rule include octahedral and square-planar complexes. The rule is not applicable to tetrahedral complexes as it does not contain 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 only at low intensities. Unsymmetrical vibrations of an octahedral complex can transiently destroy its center of symmetry and allow transitions that would otherwise be Laporte forbidden. In cases where the rule applies, the colors of the complexes are usually relatively pale. As examples, consider  $[Cu(H_2O)_6]^{2+}$  which is a rather pale blue color *vs*  $[Cu(NH_3)_4]^{2+}$  which is an intense dark blue.

# Molecular vibrations: Vibronic coupling



Vibronic coupling removes symmetry, thus allowing d-d transition to occur.

**Spin Allowed - Spin Forbidden** Any transition for which  $\Delta S \neq 0$  is *strongly* forbidden; that is, in order to be allowed, a transition must involve no change in spin state. Consider the case of the high spin d<sup>5</sup> complex  $[Mn(H_2O)_6]^{2+}$ . Electronic transition is not only Laporte forbidden but also spin forbidden. Absorptions that are doubly forbidden transitions are extremely weak. It is understandable, then, that dilute solutions of Mn(II) are colorless.

# Promotion of an electron can only proceed if the spin orientation is conserved, i.e. $\Delta S = 0$



'forbidden' transitions

**Charge-Transfer (CT) Bands.** Similar to d-d transitions, charge-transfer (CT) transitions also involve the metal d-orbitals. CT bands are observed if the energies of empty and filled ligand- and metal-centered orbitals are similar. The direction of the electron transfer is determined by the relative energy levels of these orbitals: i) Ligand-to-Metal charge transfer (LMCT) like in  $MnO_4^-$ ,  $CrO_4^{2-}$  etc. For  $MnO_4^-$ , the d-electron count on Mn(VII) is d<sup>0</sup>. The origin of the color in this species is not due to d-d transition, rather, charge transfer from  $O^{2-}$  to Mn(VII), described as LMCT band. ii) Metal-to

Ligand charge transfer (MLCT) like in  $[Fe(bpy)_3]^{2+}$ . In this complex the charge transfer occurs from Fe(II) to the empty  $\pi^*$  orbitals of bpy ligand.

Charge-Transfe	r Absorptions	
<ul> <li>Movement of electrons between metal and ligand.</li> <li>Often 1000 times stronger than d-d transition bands.</li> </ul>		
LMCT	MLCT	
• e.g. transfer of an electron from p-orbital	<ul> <li>e.g. transferred of electron from</li> </ul>	
on a choride (u symmetry) to a metal's d-	metal's d-orbital to $\pi^*$ orbital of	
orbital (g symmetry).	CO ligand	
Favourable when metal centre is in a high	<ul> <li>Favoured electron rich metal</li> </ul>	
oxidation state.	centres and those ligated by $\pi$ -	
<ul> <li>Common for π-donor ligands (F<sup>-</sup>, O<sup>2-</sup>, N<sup>3-</sup>,</li> </ul>	acceptors	
OH-)	<ul> <li>Often higher in energy (in the</li> </ul>	
<ul> <li>e.g. Colour of KMnO<sub>4</sub> (d<sup>o</sup> complex)</li> </ul>	UV region)	

Below is a table that shows typical  $\varepsilon$  values for different types of transitions.

Expected intensities of electronic transitions			
Type of transition	Typical ε /dm³ mol-1 cm-1	Example	
Spin-forbidden 'd-d'	< 1	$[Mn(OH_2)_6]^{2+} \text{ (high spin } \\ d^5\text{)}$	
Laporte-forbidden, spin-allowed 'd-d'	1-10	Centrosymmetric complexes, <i>e.g.</i> [Ti(OH <sub>2</sub> ) <sub>6</sub> ] <sup>3+</sup> (d <sup>1</sup> )	
	10-1000	Non-centrosymm. [NiCl <sub>4</sub> ] <sup>2-</sup>	
Charge transfer (fully allowed)	1000-50000	[MnO <sub>4</sub> ] <sup>2-</sup>	