

Self-Study Problems / Exam Preparation

- In what situations is the value of Δ_{oct} difficult to identify?
 - when there are multiple electronic transitions which give rise to multiple peaks in the uv-Vis spectrum, for example $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ has a d^5 ground state configuration and has seven d-d bands in its UV-vis spectrum
 - when there is a mixture of different types of ligands, σ -donor and/or π -donor and/or π -acceptor, this will also give rise to multiple energy levels and transitions, we can differentiate between the Δ_{oct} of individual ligand types and for the whole complex
 - Δ_{oct} can be taken as the maximum splitting of the dAO manifold
 - determining Δ_{oct} is difficult experimentally when the TM-complex will not dissolve (is insoluble) precluding measuring a uv-vis spectrum, or when there are solvent or contamination bands which obscure the d-d peaks in the experimental spectrum, the transition can also be very broad, in this case taking the peak maximum does not well represent the range of transitions possible, alternatively there may be two transitions which combine to form a single broad feature, with the peak maximum now between the two transition maxima, in these cases carrying out a calculation and computing the spectrum aids interpretation
- Why is it easy for the oxo ligand O^{2-} to convert between a double and triple bond with a metal?
 - The MO interaction diagram for an oxo ligand shows that there is σ -donor and π -donor FOs. O has the configuration $1s^2 2s^2 2p^4$. If we consider only the pAOs, 2e enter into the σ -donor MO there are 2e left to share over the two π -donor orbitals, if one electron is shared with metal for each MO then we have a very covalent triple bond, Figure 1.
 - However if the 2e pair up in one of the π -donor FOs then we have a double bond with strong donating character from the oxo ligand. Technically in this later case the “empty” π -orbital on O^{2-} could act as an electron acceptor via back-donation, Figure 1.
 - If the ligand is charged such as O^{2-} then all of the pAOs on the O are filled and are unable to share e with the metal, the oxo ligand is then a pure donor ligand, this would be favoured by metals in high oxidation states and low numbers of d electrons, Figure 1.
 - The reality of any bonding situation will be a “resonance” between all the options shown in Figure 1, some of which are favoured more than others. Sometimes the electrons shared by the metal are “assigned” to the ligand, and sharing makes the oxo ligand formally O^{2-} . In these interactions the M dAOs are higher in energy and so the shared electrons will spend more time on the O ligand. It is important to be clear about where the extra 2e come from!

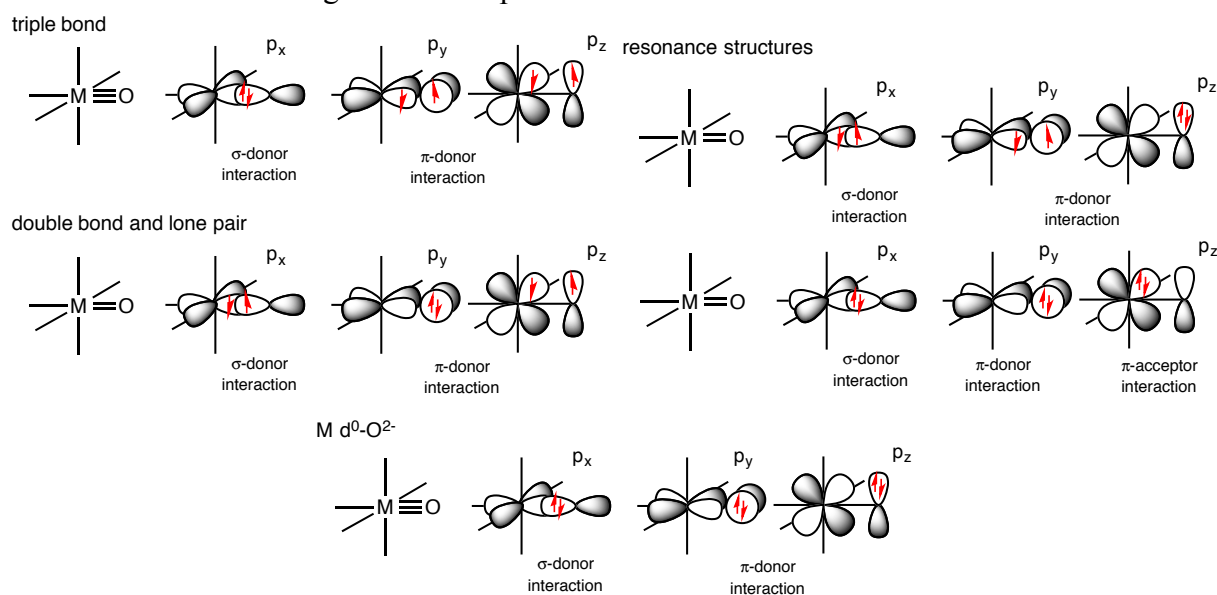


Figure 1 M-O interaction modes

- O_2 can coordinate to the the TM end on or side on, what type of ligand is O_2 in each orientation?
 - end on O_2 is like CO and is a π -acceptor ligand, however because the π^* FOs are partially occupied O_2 is a weak π -acceptor. Also because these orbitals are partially occupied O_2 could potentially act as a weak π -donor. However, O is electronegative so this is less favourable.
 - Considering the MOs alone we might think end on O_2 could be a π -donor, through the π -MOs of O_2 , however as O is very electronegative compared to a metal the π -MOs on O_2 are deeper in energy and interaction with the dAOs is not favoured.
 - side on O_2 is like an alkyne and is a δ -acceptor ligand, however because the π^* FOs are partially occupied O_2 is a weak δ -acceptor. Also because these orbitals are partially occupied O_2 could potentially act as a weak δ -donor. However, O is electronegative so this is less favourable.
- Draw out the possible dAO- O_2 ligand interactions and label each component, **Figure 2**

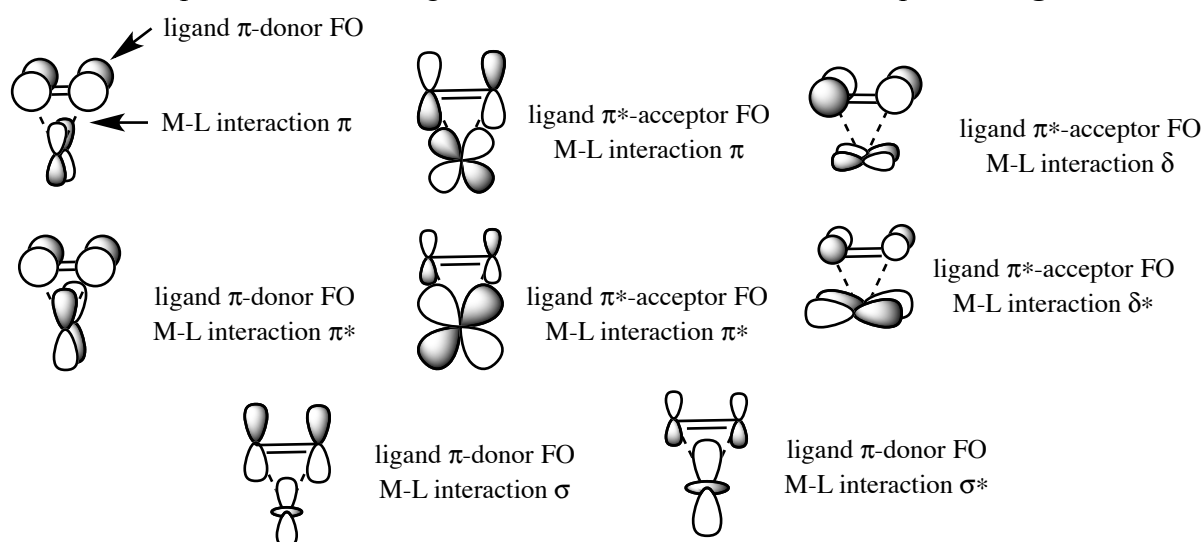


Figure 2 the various ligand FO and the M-L interaction types

- The following is information for your interest
 - nearly all TM bind dioxygen. Dioxygen can bind as a neutral molecule, as an anion (superoxide) or as the dianion (peroxide). Adding electrons to the MO diagram of O_2 is easy because in neutral O_2 the HOMO is a degenerate set of π^* orbitals with only two electrons. Adding 1e or 2e into an antibonding π^* orbital reduces the bond order for example bond distances (O-O) of O_2 , O_2^- and O_2^{2-} are 1.21, 1.33 and 1.49 Å respectively.
 - isolated dioxygen has triplet character, this is changed to singlet on coordination to a TM, when O_2 formally accepts 1e (O_2^{1-}) and exhibits O-O double bond character it is called a superoxo ligand. When O_2 formally accepts 2e (O_2^{2-}) and exhibits O-O single bond character it is called a peroxo ligand. In both cases oxygen is reduced while the TM is oxidised.
 - the binding of oxygen is particularly interesting in the context of biology, as myoglobin and hemoglobin. In addition O_2 has widespread application in oxidation catalysts, and is of particular interest because dioxygen is “green” as it is freely available in the atmosphere. However, there are problems as the reactivity is difficult to control (combustion occurs!), reactions can be difficult to initiate due to the triplet character of O_2 and often an atom of oxygen is retained following oxidation.
 - X-ray diffraction can be problematic because the dioxygen is closely bound to the metal the exact location of the atoms are difficult to locate due to the large electron density of the metal. Often other methods are employed to confirm the structure, including IR and Raman studies of the O-O bond stretching frequencies and theoretical calculations. In a complex the superoxide is $\approx 1100\text{--}1200\text{cm}^{-1}$ and the peroxide O_2^{2-} is $\approx 800\text{--}900\text{cm}^{-1}$.
 - O_2 is often found as a bridging ligand, **Figure 3**

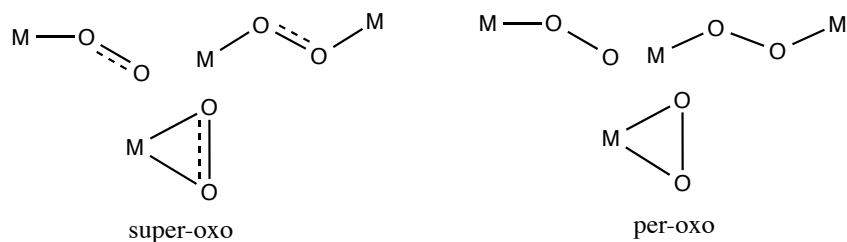
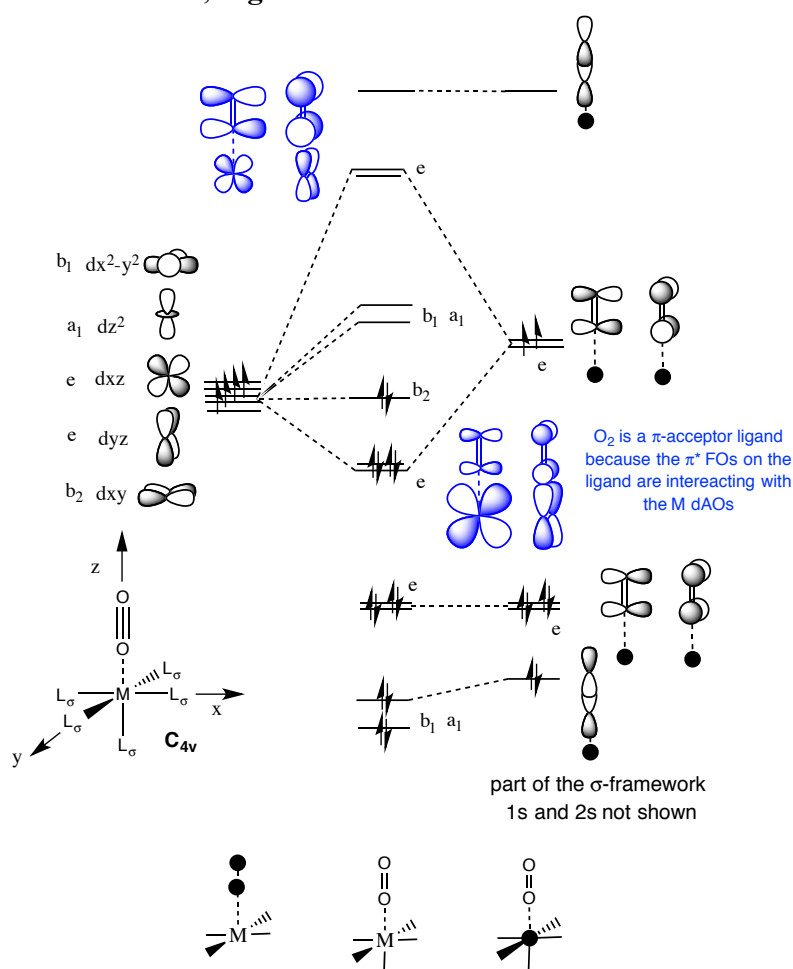


Figure 3 dioxygen bound end on or side-on

- Draw the relevant MOs for O_2 coordinated to a TM end on (linear), clearly show what type of ligand O_2 is for this orientation, **Figure 4**

Figure 4 The key MOs for O_2^{2-} interaction end on

- Extra for experts! What happens to the MO diagram when the O_2 bends away from linear?
 - Dioxygen can bind end-on, however the end-on complex is not normally linear but is bent, the end on bent conformation is generally favoured.
 - When a ligand of the type X_2 interacts with a metal, there is a dAO- $L\pi^*$ interaction. If this interaction is strong the X-X bond is reduced while strengthening the M-X interaction, **Figure 5a** Thus there is a subtle interplay between the stability of these two bonds and the geometry favoured.
 - the nitrosyl ligand (NO) has one more electron than CO and the O_2 ligand which has two more electrons than CO, can form linear or bent bonds, depending on the extent of interaction with a TM. CO and N_2 which have no electrons in the π^* FOs prefer a linear end on coordination, , **Figure 5b**
 - When the M- X_2 bond bends there is a drop in symmetry, causing the e MOs to no-longer be degenerate and allowing mixing. In particular the unoccupied a' of the dz^2 M- $L\sigma^*$ will be

able to mix with the partially occupied dxz M-L π^* MO dropping the energy of the dxz M-L π^* MO slightly, **Figure 5c**.

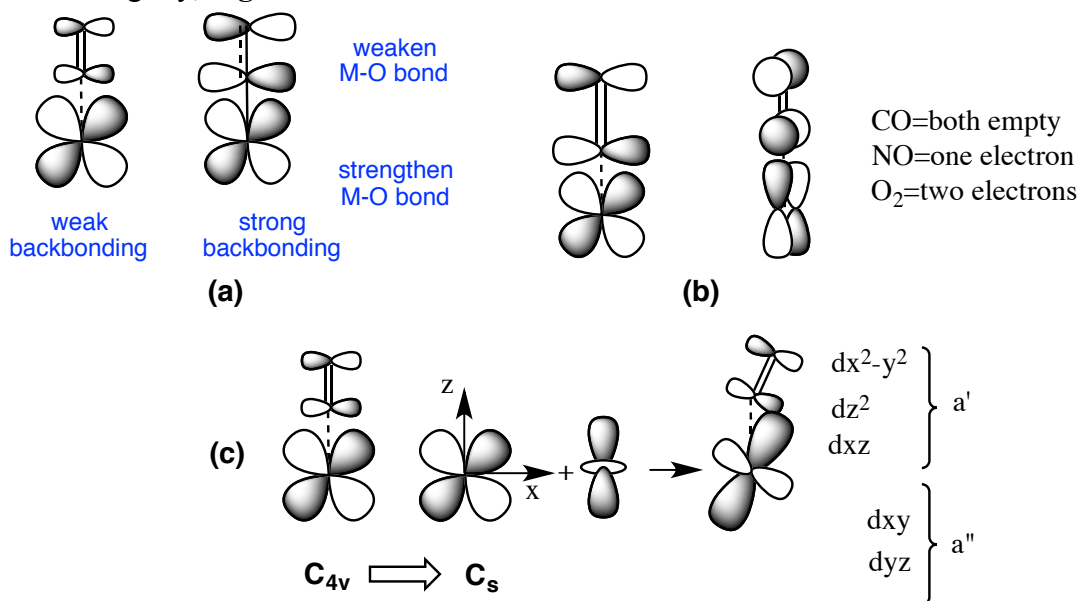


Figure 5 bent vs linear end-on coordination

- deciding on an oxidation state can be complex once you understand the MO interactions, as the two approaches do not always match up!
 - NO has 1e in the π^* -FOs (and the σ -FO interaction is counted as 2e donation)
 - when NO is linear, alignment with the π^* -FO means back-donation can be maximised, however in this case NO is assumed to be NO^+ (isoelectronic with CO) and formally forms M^-NO^+ (π^* -FO 0e) where NO has donated 1e to the M (thus the metal is reduced).
 - when NO is bent, mixing occurs, because the orbitals mixing are dominated by the dAOs this mixing is emphasised, however the ligand NO FOs mix as well (forming a σ^*/π^* -mixed orbital). The situation is complex and a calculation is generally the best way to proceed. However, formally in terms of Lewis structures the NO is assumed to be NO^- (isoelectronic with O_2) forming M^+NO^- (σ^*/π^* -mixed orbital has 2e) where NO has accepted 1e from the M (thus the metal is oxidised)
 - this illustrates that formal oxidation states are just that a *formalism* used by chemists before they understood MO theory. MO theory is complex and chemists need a quick and easy way to think about TM-ligand interactions, formal oxidation states help do this. I find it easiest to not ask one theory to justify or inform on the other. MOs have little to do with formal oxidation states and formal oxidation states have little to do with MO theory. These are two ways of approaching the same problem, the more information we have, and the more ways we have of thinking about a problem the better.

Draw the relevant MOs for O_2 coordinated side-on to a TM, clearly show what type of ligand O_2 is for this orientation, **Figure 6**

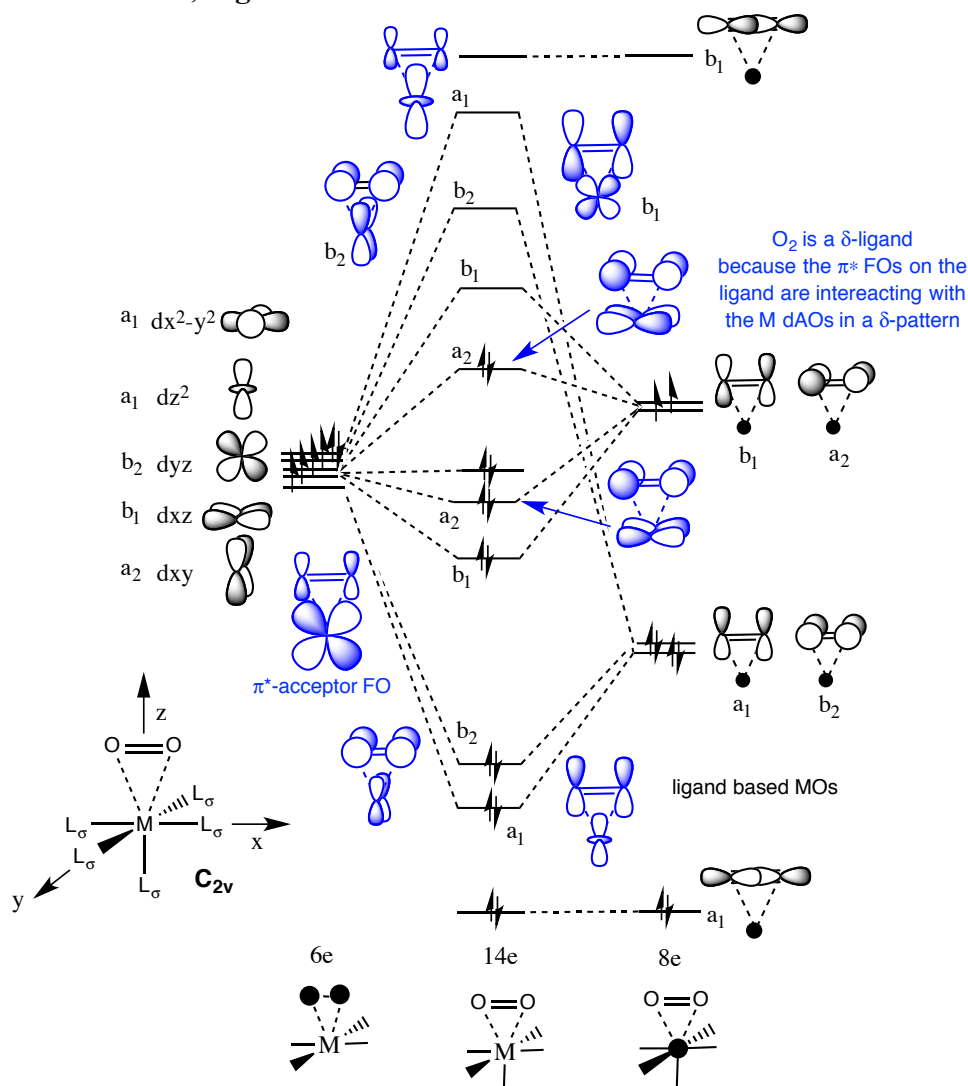
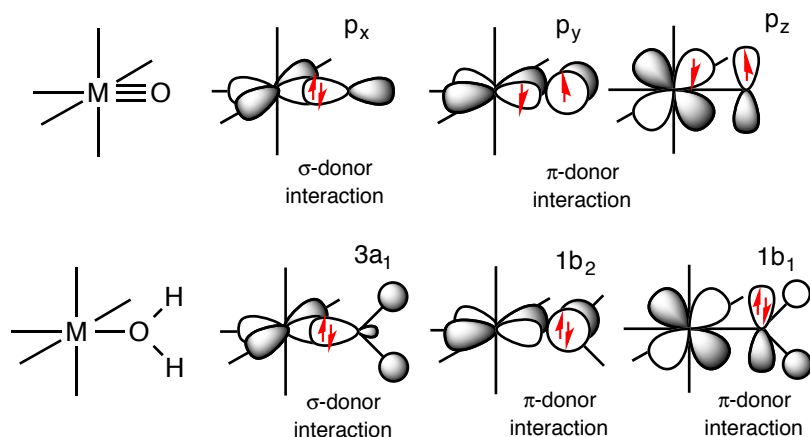


Figure 6 The key MOs for O_2 interaction side-on

- What type of ligand is H_2O ? Draw a diagram showing the $M-OH_2$ orbitals that will interact. Explain the dichotomy of H_2O being a stronger field ligand than O_2^{2-} .
 - H_2O is strong σ -donor and weak π -donor ligand, hence it is often classed as a σ -donor ligand.
 - the polarisation of the $3a_1$ MO means there is a strong σ -overlap and makes H_2O a good σ -donor
 - in the following I will keep the C_{2v} notation for an isolated water molecule to enable us to discuss the energy levels and orbital interactions relative to the water molecule. In the complex the z-axis changes and so (in terms of the complex) the orbital labels will change.
 - the $1b_1$ MO has the correct symmetry to behave as π -donor FO. However, this FO lies even deeper in energy than the $3a_1$ MO and has electrons delocalised over the whole MO, thus the energy match with the dAOs is poor, and overlap density with the metal is reduced, this MO only forms a weak π -donor interaction.
 - the $1b_2$ (HOMO) is a non-bonding pAO and very similar to the p_y in O_2^{2-} and forms a stronger π -donor interaction.
 - compared to O_2^{2-} which has 2 strong π -donor interactions, H_2O has one poor π -donor FO (b_1) and one stronger π -donor FO (b_2), thus compared to O_2^{2-} H_2O is a weaker π -donor, **Figure 7**.
 - crystal field theory would suggest that as O_2^{2-} is negatively charged and H_2O is neutral that O_2^{2-} should be the stronger field ligand, however empirical evidence of the spectrochemical series shows the reverse.

- in the spectrochemical series $O^{2-} < H_2O$ this is because O^{2-} has strong π -donation via both pAOs raising the e_g^* energy and reducing Δ_{oct} . H_2O is a weak π -donor this lowers the e_g^* energy increasing Δ_{oct} compared to O^{2-} .
- the non-bonding nature of the $1b_2$ should mean the top “ e_g^* ” MO is shifted a similar amount in O_2 . However Δ_{oct} is maximum span of the dAOs, thus we are concerned with the smallest shift in the energy of the “ e_g^* ”, and so it is the $1b_1$ interaction that is important for determining Δ_{oct} for H_2O (see the answer to the next question for an energy level diagram).

Figure 7 O^{2-} and H_2O interaction modes

- Extra for experts! Explain using MO theory and diagrams why $cis-[CoCl_2(NH_3)_4]^+$ is violet and $trans-[CoCl_2(NH_3)_4]^+$ is green.
 - NH_3 is a σ -donor ligand and Cl is a π -donor ligand
 - first work out the d electron count and oxidation state of the metal: Co is in group 9 which means d^9 as neutral metal, the $2Cl$ ligands are -1 each, the NH_3 is a 0 acceptor, and there is a positive charge removing another electron thus this is Co(III) and the complex is d^6 .
 - a violet colour of $cis-[CoCl_2(NH_3)_4]^+$ means the complex absorbs in the yellow region $\approx 570nm$ and a green colour of $trans-[CoCl_2(NH_3)_4]^+$ means that the complex absorbs in the red region $\approx 680nm$, thus $trans-[CoCl_2(NH_3)_4]^+$ has a smaller Δ_{oct} than $cis-[CoCl_2(NH_3)_4]^+$
 - because these are a mixed σ -donor/ π -donor complex there will be multiple contributions to the spectra however the lowest energy transition will be to dAOs interacting with the π -donor ligands and this will dominate in determining Δ_{oct}
 - the π -donor interaction reduces Δ_{oct} by raising the “ e_g ” MOs, **Figure 8**
 - however we need to consider the combination of the two sets of ligand π -donor orbitals, representative diagrams are given below, be careful about choosing the axes, **Figure 8**
 - as the ligand FOs are far apart their interaction will shift the energy levels only slightly from the p_x and p_y , however the π^* -ligand combination will lie slightly higher than the π -ligand combination allowing it to interact slightly better with the metal because the energy difference between the FOs is less.
 - the cis -ligands are actually closer together and have an unimpeded through space interaction, which means they will interact more pushing the π^* ligand pair up even higher and the π ligand pair down lower.
 - however ΔE is not the only consideration and the extent of orbital overlap must also be considered. In $trans-[CoCl_2(NH_3)_4]^+$ the π^* -ligand combination interacts very favourably with the metal dAOs, however in $cis-[CoCl_2(NH_3)_4]^+$ the FOs within the equatorial plane for cis -conformer do not overlap effectively with the available dAOs.
 - in this case the very favourable overlap of the $trans$ -ligands could be considered to dominate, thus in $trans-[CoCl_2(NH_3)_4]^+$ the π^* -ligand combination interacts best with the metal dAOs, pushing the “ e_g ” MOs up by the greatest amount and thus reducing Δ_{oct} the most.

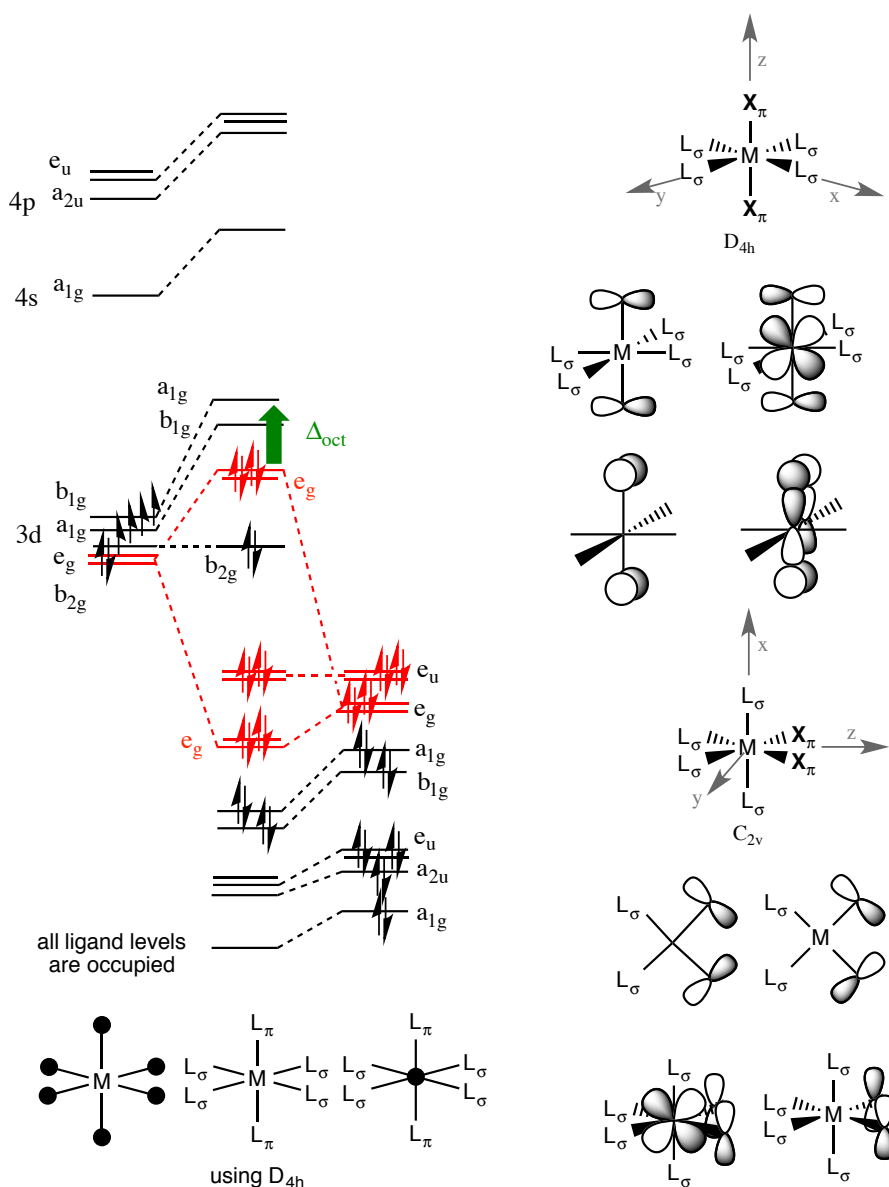


Figure 8 cis vs trans isomers and the effect on Δ_{oct}

- while this explanation provides a rationalisation for the colour differences between trans- and cis- $[\text{CoCl}_2(\text{NH}_3)_4]^+$ the reality is more complex, non-bonding ligand orbitals lie in this region, moreover the effect of the differing σ -donor orbitals for NH_3 vs Cl make a difference to the antibonding a_{1g} and b_{1g} levels. Calculation combined with experiment is needed to best understand the electronic structure of even simple complexes like these! The important point is that we would not have a handle on what is happening electronically if we did not understand the basic electronic structure of octahedral and related complexes.
- have a look at the computed orbitals for the two conformers using the *.fchk files supplied on-line.
- Form the energy diagram for a complex ML_4X_2 where $\text{L} = \sigma$ -bonding ligand and X are π -donor ligands positioned axially. Include diagrams of the key MOs.
 - please see the hand-drawn answer on-line as a pdf