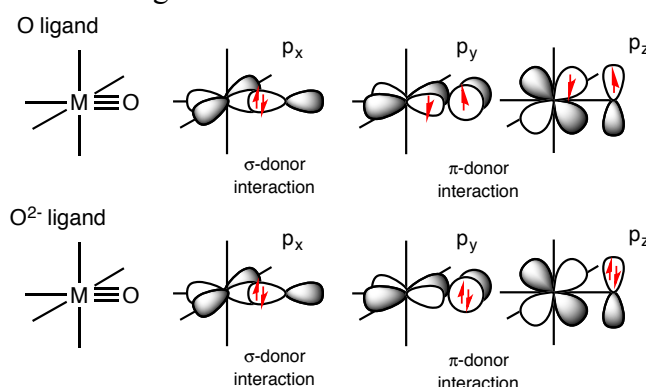


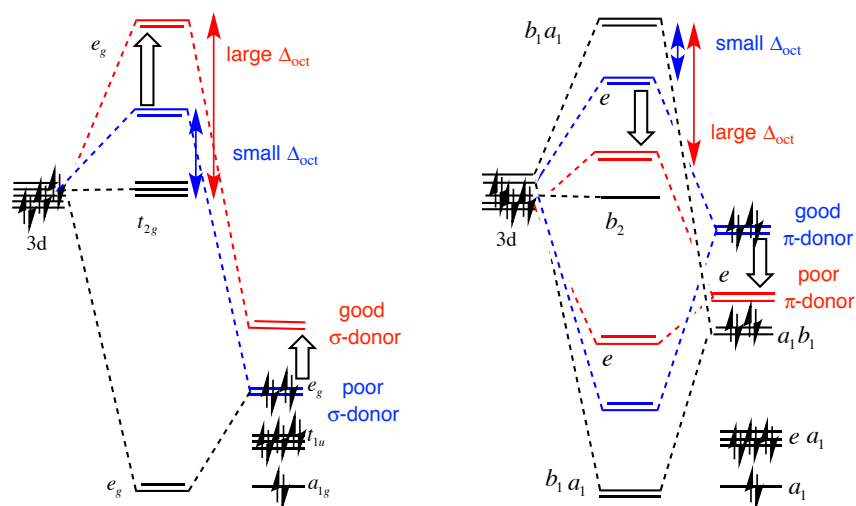
In-Class Activity

- what type of ligand is  $O^{2-}$ ?
- Draw a diagram showing metal dAOs and  $O^{2-}$  FOs interacting (ie the MOs).
  - O has 4p valence electrons and can interact with filled dAOs on a TM, because of the electronegativity of O the MOs formed are dominated by the O contribution, and the electrons can be formally considered to reside on the O ligand ( $O \rightarrow O^{2-}$ ) while M is oxidised ( $M > M^{2+}$ ), **Figure 1**.
  - It is also possible for a TM with no d electrons to interact with  $O^{2-}$  which has 6p valence electrons, **Figure 1**. We can also think of these two options as resonance structures both contributing to the real bonding situation.



**Figure 1** Diagram showing the orbital interactions for O and  $O^{2-}$

- $O^{2-}$  is a strong  $\pi$ -donor ligand because the pAOs can donate into empty dAOs.  $O^{2-}$  is a weak  $\sigma$ -donor because the high electronegativity of oxygen means that the bonding  $\sigma$ -MO is strongly dominated by the s-FO contribution.  $O^{2-}$  cannot be a  $\pi$ -acceptor because there are no  $\pi^*$  FOs in this ligand
- If a complex has only  $\sigma$ -donor ligands how is  $\Delta_{oct}$  increased?
  - add a ligand which has higher energy FOs that will form a strong antibonding interaction with the metal dAOs and hence strongly raise the antibonding “ $e_g$ ” MOs increasing  $\Delta_{oct}$ , **Figure 2a**



**Figure 2** Diagram showing changes to  $\Delta_{oct}$

- If a complex contains a  $\pi$ -donor ligand how is  $\Delta_{oct}$  maximised?
- add a small electronegative  $\pi$ -donor ligand which has lower energy FOs that will form a weak antibonding interaction with the metal dAOs raising only slightly some of the “ $t_{2g}$ ” MOs thus maximising  $\Delta_{oct}$ , **Figure 2b**