

Week 7

Bonding in Coordination Complexes

7.1 Coordination Complexes: π Bonding and all- σ Distortions

11/7:

- Video lecture Wed and Fri; watch by Mon and have questions.
- Last time: MO diagram for an ML_6 coordination complex whose ligands only engage in σ interactions.
- Today: The case where the ligands also have π orbitals.
- As per usual, we follow the procedure from Lecture 6.1.
 1. Point group: O_h .
 2. Assigning coordinate axes is a bit more complicated here, but the following will work.

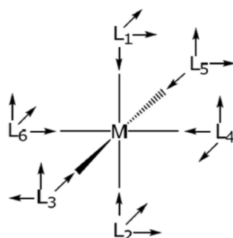


Figure 7.1: ML_6 π xyz coordinates.

- We have two orthogonal $p\pi$ bonds.
 - The arrows indicate the directional phase of the p orbitals.
3. Let's create a representation for the 12 p orbitals capable of π bonding.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$\Gamma_{12\pi}$	12	0	0	0	-4	0	0	0	0	0

Table 7.1: Representation for the $p\pi$ ligand orbitals of ML_6 .

4. Reducing, we get

$$\Gamma_{12\pi} = T_{1g} + T_{1u} + T_{2g} + T_{2u}$$

5. From Table 6.8, the atomic orbitals of the metal transform as

$$s \sim a_{1g} \quad p_x, p_y, p_z \sim t_{1u} \quad d_{z^2}, d_{x^2-y^2} \sim e_g \quad d_{xz}, d_{yz}, d_{xy} \sim t_{2g}$$

- Thus, the metal p and d_{xz}, d_{yz}, d_{xy} orbitals interact with the ligand π SALCS.

6. Once again, we can “guess” the SALCs based on experience.

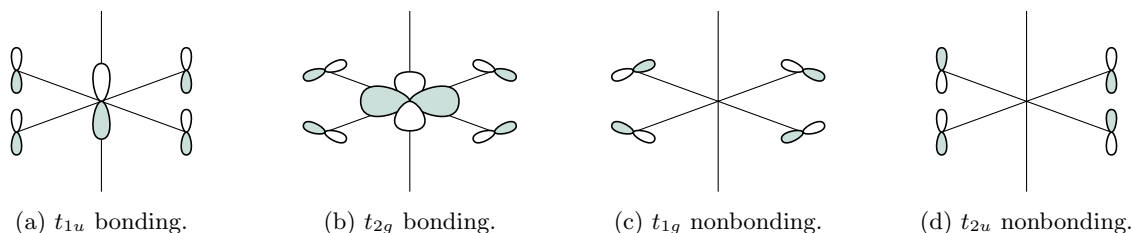


Figure 7.2: ML_6 π SALCs.

– In addition to these, there are two more (oriented along the other orthogonal coordinate axes) for each IRR.

7. We can now make sense of the MO diagram.

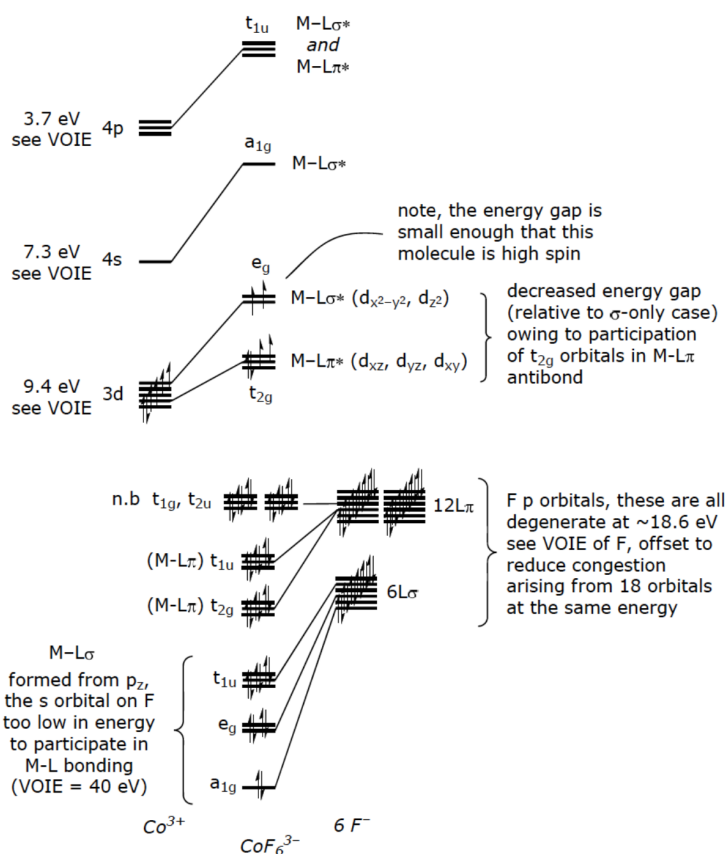
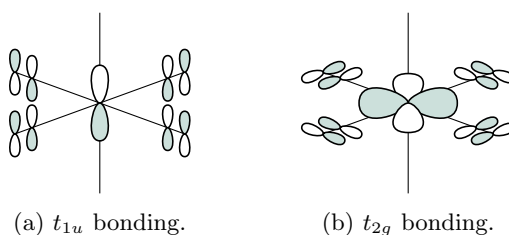


Figure 7.3: ML_6 π MO diagram.

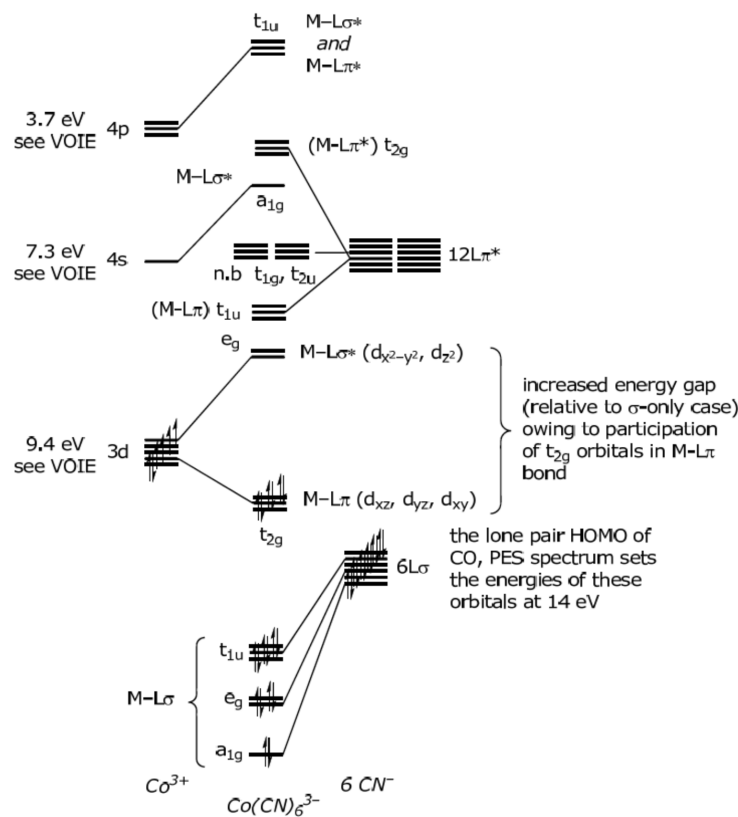
- Wuttig compares this MO diagram to the all- σ case (Figure 6.13).
 - The M-L σ and M-L σ^* distortions stay the same; we now just have *additional* M-L π and M-L π^* distortions to consider.
 - π -donating ligands, such as the fluoride ligands causing the interactions in Figure 7.3, *raise* the t_{2g} set in energy; they contribute *antibonding* interactions.
 - Note that the L π orbitals sit above the L σ orbitals.
- Wuttig probably expects us to be familiar with the M-L π^* notation.

- It seems that now we're done. But wait: We have made an assumption that is not necessarily justified in every case.
 - We have treated the ligand as a point particle with atomic orbitals that mirror the metal center (i.e., your typical s , p , etc. orbitals).
 - This is justified in the case of fluoride (as in Figure 7.3). But what about a ligand such as carbon monoxide? CO certainly has molecular orbitals more complicated than the atomic orbitals of either carbon or oxygen alone, so is it still valid to treat it as a point particle with “atomic” orbitals?
 - In fact, it is not, and we will now see how to treat that case.
- As with fluoride, the frontier orbitals of CO will be the ones that interact with the metal center.
- To draw SALCs of the interactions of these MOs with the metal center, we need to know what *they* look like first. Fortunately, we have encountered the SALCs for heteronuclear diatomics before, and we can simply use these as our basis set to draw the overall SALCs.

Figure 7.4: $M(\text{CO})_6$ π -bonding SALCs.

- Wuttig draws the Figure 7.4a interactions in-plane, too, though??
- Wuttig also doesn't draw the nonbonding ones, but they still exist??
- To reiterate, the π^* orbitals of CO will participate in t_{1u} and t_{2g} bonding interactions, and t_{1g} and t_{2u} nonbonding interactions just like the p orbitals of F; it is *strictly* and *solely* the basis set that we're changing.
- An additional complication arises from the fact that the frontier orbitals of CO are fundamentally different than those of F.
 - In particular, the frontier orbitals of F are filled π -donating atomic orbitals, while CO has a filled σ -donating frontier orbital (HOMO) and an unfilled π^* -accepting frontier orbital (LUMO).
 - Thus, we need to consider the new *energetics* of these orbitals as well.
 - For a π -donating ligand such as monoatomic fluoride, the σ and π orbitals are degenerate.
 - This is because all 18 ligand orbitals come from the $2p$ *atomic* orbitals of fluorine.
 - However...
- Are the σ and π orbitals of the π -accepting ligands degenerate in energy?
 - They are not.
 - This is because we are considering the interactions of nondegenerate ligand *molecular* orbitals with the metal center.
 - Evidence: We can inspect the photoelectron spectrum of our ligand (e.g., for CO, we observe distinct peaks corresponding to its σ -donating and π^* -accepting orbitals).
 - Note that ligands such as CO still have filled π MOs; it's just that these lie so low in energy that they don't interact with the metal center.

- The consequence of this is that the π ligand orbitals of a π -accepting ligand lie significantly higher in energy.
 - In fact, they lie higher in energy than a metal's d orbitals, meaning that the metal t_{2g} set is now M-L π bonding instead of antibonding and hence lower in energy, leading to a greater d orbital splitting.
- All of this can be summarized by the MO diagram for a ML_6 complex with π -accepting ligands.

Figure 7.5: ML_6 π -accepting MO diagram.

- Distortions from σ interactions.
- Consider a ML_6 complex with σ -only interactions, as discussed last class.
 - Goal: Predict Jahn-Teller distortions from first principles.
 - Two possible distortions: A tetragonal compression or a Jahn-Teller elongation.
 - See Figure VI.10 of Labalme (2022).
 - Are both of these distortions not “Jahn-Teller” effects??
 - Either distortion changes the point group from O_h to D_{4h} .
- We now seek to build an MO diagram for the t_{2g} and e_g set of each distortion.
 - To begin, we determine the symmetries are the d orbitals in the two point groups (see Table 7.2).
 - Since the t_{2g} set is nonbonding in a σ -only complex, their energy doesn't change much, so the distorted t_{2g} set is basically still degenerate. However, we do have to draw the b_{2g} MO slightly higher (or lower, but we choose higher) since it has a different symmetry.

	O_h	D_{4h}
$d_{x^2-y^2}$	e_g	b_{1g}
d_{z^2}	e_g	a_{1g}
d_{xy}	t_{2g}	b_{2g}
d_{yz}	t_{2g}	e_g
d_{xz}	t_{2g}	e_g

Table 7.2: d -orbital symmetries in O_h vs. D_{4h} .

- The e_g orbitals definitively split, going in different directions as the axial ligands compress or expand. In particular, compressing the axial ligands drives d_{z^2} up (and $d_{x^2-y^2}$ down), and vice versa for expanding the axial ligands.
- Note that the original e_g set is $M-L\sigma^*$, which is why compression drives up energy (more mixing between regions of opposite phases is not energetically favorable).

7.2 Descent in Symmetry

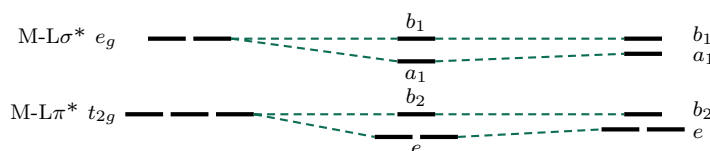
- 11/9:
- Goal: Consequences of distortion and descent in symmetry on the MOs of coordination complexes.
 - **Homoleptic:** A coordination complex, the ligands of which are all identical.
 - **Heteroleptic:** A coordination complex containing at least two distinct ligands.
 - Most interesting chemistry occurs for heteroleptics, so we should consider their MOs, too.
 - But how do we construct such molecular orbitals? Use a Descent in Symmetry Analysis.
 - Similar to the Jahn-Teller distortion and tetragonal compression discussed in Lecture 16, but now we're taking this a step further by fully removing ligands. We then investigate the effects of this on orbital energetics.
 - How do the symmetries of the d orbitals compare from $Co(CN)_6$ to the hypothetical “chopped off $Co(CN)_5$ complex,” i.e., C_{4v} fragment?
 - We rip a cyano group off of the axial position and will substitute a bromo group later.
 - Changing from O_h to C_{4v} involves a change in the symmetries of the orbitals, as follows.

	O_h	C_{4v}
$d_{x^2-y^2}$	e_g	b_1
d_{z^2}	e_g	a_1
d_{xz}	t_{2g}	e
d_{yz}	t_{2g}	e
d_{xy}	t_{2g}	b_2

Table 7.3: d -orbital symmetries in O_h vs. C_{4v} .

- Taking a π -acceptor off of the z -axis won't affect $d_{x^2-y^2}$; we just change the label from $e_g \mapsto b_1$.
- Since d_{z^2} now has a less productive σ -bonding interaction, the $M-L\sigma^*$ d_{z^2} orbital decreases in energy (and changes to a_1).
- As with $d_{x^2-y^2}$, d_{xy} doesn't change except in symmetry.
- Analogously to d_{z^2} , d_{xz} and d_{yz} now increase in energy because we lose the stabilizing effect of the π^* ligand acceptance.

- Now what happens when we add Br^- back in?
 - Br^- is a π -donor!
 - Quantitatively, we need to find the symmetry of the Br^- atomic orbitals and mix them with the MOs of the fragment.
 - Since p_z has a_1 symmetry, it can interact with the d_{z^2} orbital of Co. Thus, it will be $\text{M-L}\sigma^*$ with respect to the metal, and $\text{M-L}\sigma$ with respect to the Br^- .
 - p_x, p_y have e symmetry. Thus, they can interact with d_{xz}, d_{yz} of the metal via $\text{M-L}\pi^*$ interactions, raising the e set higher.
- Key point: Bonding character is mixed in heteroleptics because MOs have multiple parentage. Let's build the MO for the target complex now.
 - The a_1 and e sets of the $\text{Co}(\text{CN})_5$ fragment are both raised in energy.
 - We see multiple parentage in the e set, for instance, where we have $\text{M-L}\pi$ interactions with cyano ligands and $\text{M-L}\pi^*$ interactions with the bromo ligand.
 - Cyano ligands act as stabilizing π -acceptors on d_{xz}, d_{yz} .
 - Bromo ligands act as destabilizing π -donors on d_{xz}, d_{yz} .
 - We fill in 6 d electrons for $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ because such a structure implies Co^{3+} , which has 6 d electrons.
- Example: NbCl_5O .

Figure 7.6: NbCl_5O d orbitals derivation.

- Remove a π -donor; add back another π -donor.
- Thus, we drop the e and a_1 sets, and then raise them back up (but not all the way to degeneracy).
- The $\text{M-L}\sigma^*$ notation denotes molecular orbital **parentage**!
- Further descents in symmetry: Two ligands gone means D_{4h} ; three ligands gone means C_{2v} .

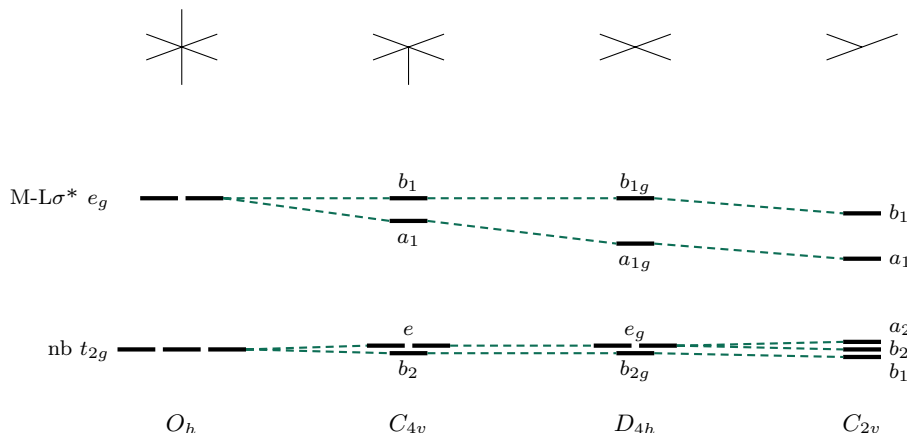


Figure 7.7: Full descent in symmetry.

- Wuttig considers the σ -only case here.
- D_{4h} : Another z σ -donor gone lowers $a_1 \mapsto a_{1g}$ further.
- C_{2v} : Fewer z donors means lower a_1 . Fewer xy -donors means lower b_1 . The nonbonding t_{2g} set is still unchanged.

7.3 Metal-Metal Bonding

- 11/11:
- Picking up from last time with Walsh diagrams; we'll get to metal-metal bonding later.
 - Last time, we talked about descents in symmetry from one particular point group to another destination point group.
 - Today: What about intermediate geometries that don't quite fit any particular point group?
 - We use **Walsh diagrams** to treat these cases.
 - **Walsh diagram**: A plot of orbital energy vs. a measure of distortion, often the angle θ between some bonds.
 - Let's look at an example of a Walsh diagram. We'll break down how and when to build one, and what information we can glean from one.
 - Consider a square pyramidal C_{4v} complex.

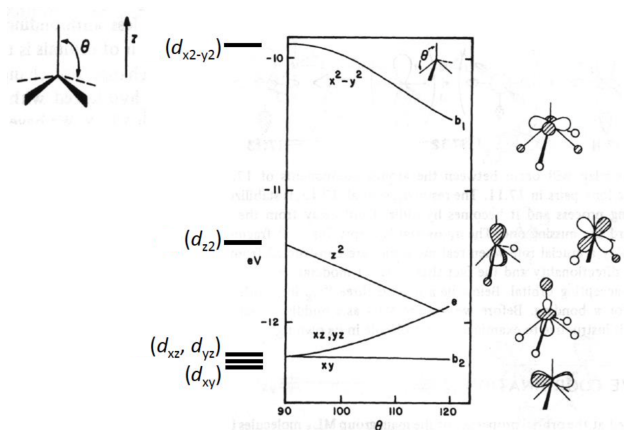
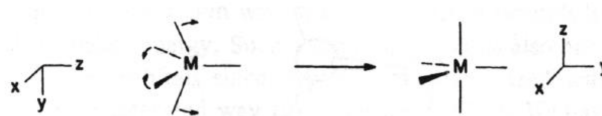


Figure 7.8: Walsh diagram for the distortion of a C_{4v} coordination complex.

- As we increase the angle between the axial ligand and each equatorial ligand, we remain in the C_{4v} point group, but we have changes among orbital energy, too.
- Derive one side, then the other side, and then draw a line connecting the two analogous orbitals.
- A benefit of Walsh diagrams: They allow us to predict the distortion as a function of electron count.
- Continuing with the C_{4v} example in Figure 7.8...
 - For d^0 - d^2 , steric pressures imply a distorted pyramid; electronic stability isn't significant.
 - For d^3 - d^6 , however, we can expect a flat pyramid since the orbitals that are now being filled (d_{xz}, d_{yz} of e symmetry) are destabilized in the distorted geometry. In fact, the more electrons we add, the stronger the preference for flat.
 - For d^7 - d^8 , the equilibrium shifts back toward distortion ($x^2 - y^2$ gets stabilized by distortion).
 - For d^9 - d^{10} , the distortion grows even more rapidly (z^2 also gets stabilized by distortion).

- What happens when the principal rotation axis is not preserved as a function of descending symmetry?
- Consider the case where we go from distorted C_{4v} to trigonal bipyramidal (D_{3h}).

Figure 7.9: Distortion from C_{4v} to D_{3h} .

- In a nutshell, we must derive d -orbital manifolds in both point groups and connect them just like before, but we now have the additional challenge of orbital labels changing. Let's begin.
- Note that not only does the point group change here, but we are forced to reorient the axes if we want to keep the z -axis as the principal axis.
- Once again, we assume σ -only interactions.
- Determine what axis maps to what other axis: $x \mapsto x$, $z \mapsto y$, and $y \mapsto z$.
 - Note that we don't send $y \mapsto -z$ because we are only interested in direction (mapping *axes* to *axes*), not intra-basis orientation.
- Drawing a Walsh diagram for the case we've been discussing.

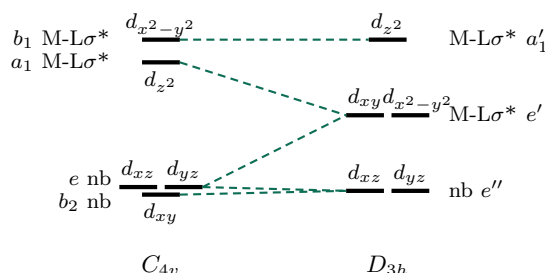


Figure 7.10: Walsh diagram when the principal axis is not preserved.

- Start with the C_{4v} d -orbital manifold on the left and the D_{3h} d -orbital manifold on the right.
- Be cognizant of the fact that we have to relabel orbitals because we relabeled axes! Indeed, $d_{xy} \mapsto d_{xz}$, $d_{yz} \mapsto d_{yz}$, and $d_{xz} \mapsto d_{xy}$.
 - Thus, what we call the d_{xz} orbital on the right (for example) is literally the d_{xy} orbital on the left.
- Wuttig rationalizes the D_{3h} splitting using the ligand SALCs and their symmetries.
 - For the D_{3h} molecule, the ligand SALCS transform as

D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{L-\sigma}$	5	2	1	3	0	3

Table 7.4: Representations for the $L\sigma$ orbitals of a D_{3h} complex.

i.e.,

$$\Gamma_{L-\sigma} = 2a'_1 + e' + a''_2$$

- The a''_2 SALCs are nonbonding, but e' and a'_1 both have $M-L\sigma^*$ interactions.
- How did Wuttig determine which of $d_{x^2-y^2}$ and d_{z^2} went to which product orbitals??

- Connect like orbitals with lines.
- Using MO theory to predict if complexes containing NO as a ligand prefer bent or linear NO.

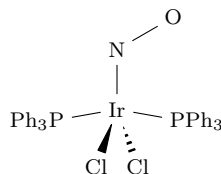
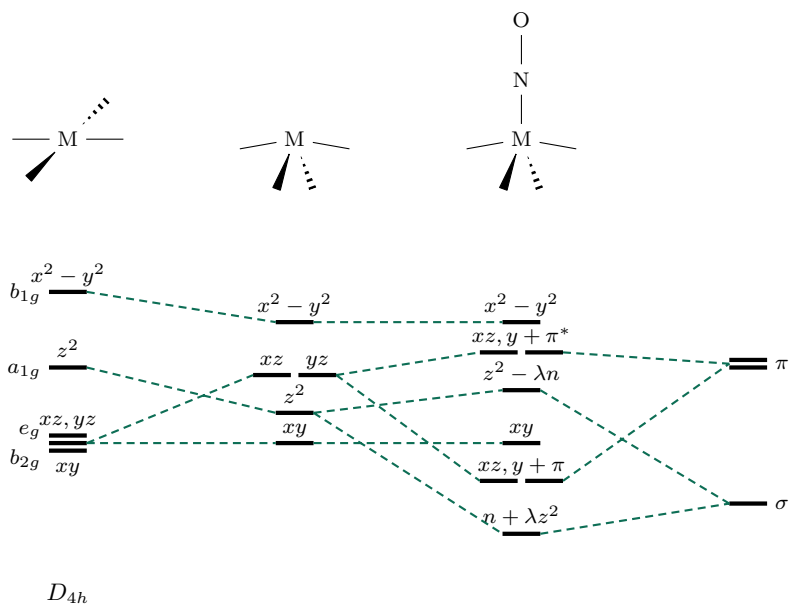


Figure 7.11: An NO complex.

- Strategy.
 1. Pyramidalize D_{4h} : Derive the MO diagram for just the $\text{Ir}(\text{PPh}_3)_2\text{Cl}_2$ ligands, assuming all ligands are the same.
 2. Combine with NO orbitals.
 3. Bend NO.
- Completing the example in Figure 7.11.

Figure 7.12: $\text{Ir}(\text{PPh}_3)_2\text{Cl}_2(\text{NO})$ MOs.

- Generalize all ligands to a generic π -donor (like Cl^-).
- Pyramidalize the molecular fragment to the D_{4h} molecular geometry.
- Give the d -orbital splitting for this point group.
- Bend the molecule and change the orbital energies accordingly: Loss of planar antibonding interactions lowers $d_{x^2-y^2}$ and d_{z^2} , loss of σ_h increases d_{xz}, d_{yz} , no change in symmetry about the principal axis means that d_{xy} is unaffected.
- These orbitals can be mixed with the linear NO frontier orbitals (a high-lying π^* one and a low-lying σ one) to generate an initial MO diagram.
- We can use a Walsh diagram to describe the distortion in the MO diagram in Figure 7.12 as we bend the NO ligand.

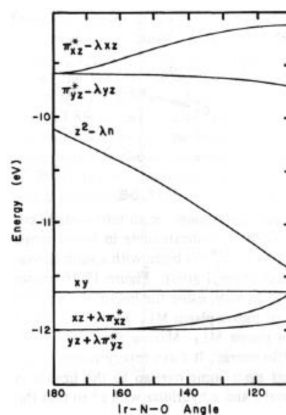
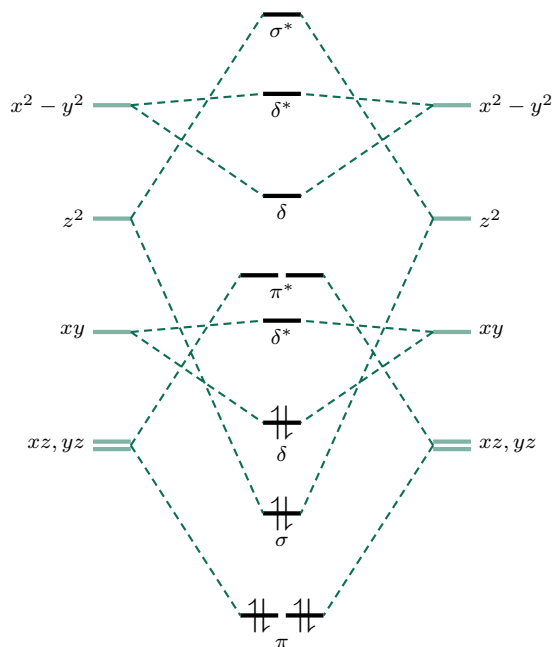


Figure 7.13: Walsh diagram for varying Ir-N-O bond angles.

- Do d^6 , d^7 , and d^8 prefer linear or bent geometries?
 - d^6 prefers linear since those orbitals lie lower in energy.
 - d^7 prefers bent for the same reason (we now have an electron in the drastically changing $z^2 - \lambda_n$).
 - d^8 prefers an intermediate angle, even though we would expect fully bent based on the Walsh diagram.
- We now move to metal-metal bonding.
- Metal-metal bonding involves δ bonds.
 - Different types of $d-d$ molecular orbitals are shown (see Figure III.8 of Labalme (2022)).
- Seminal work of Al Cotton, a giant of inorganic chemistry: One of the first quadruple-bonded complexes, $[\text{Re}_2\text{Cl}_8]^{2-}$.
- Investigating the bond-order for the Re-Re bond.

Figure 7.14: $[\text{Re}_2\text{Cl}_8]^{2-}$ MOs.

- Denote the Re–Re axis as the z -axis.
 - We form two C_{4v} ReCl_4 fragments. Their d -orbital splitting (we only care about the d -orbitals of the metal centers since we're trying to investigate the Re–Re bond) mirrors that in Figure 7.6.
 - Note that since the d_{xy}, d_{xz}, d_{yz} orbitals are $\text{M-L}\pi^*$, they are less antibonding than in the octahedral case because we no longer have the π^* contribution from the orbitals along the z -axis??
 - We then mix their identical orbitals.
 - Filling in the d -electrons on the two Re^{3+} species, we see that B.O. = 4.
- $\sigma > \pi > \delta$ in terms of bond strength and MO splitting.