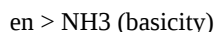


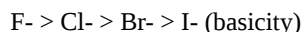
8.4.2: The Spectrochemical Series

The spectrochemical series was determined through an examination of the absorption spectra of a series of octahedral Co(III) complexes by Tsuchida in the 1930's. The position of the d-d absorption band is influenced by the field strength of the ligand, which leads to greater or lesser values of Δ_o . That interaction depends on both the relative energies of the metal and ligand orbitals and the degree of overlap between these orbitals. The closer in energy the two orbitals are to each other, the greater the interaction. Also, the greater the overlap between the two orbitals, the greater the interaction.

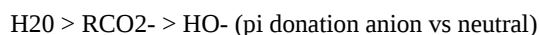
Recall that sigma donors simply donate a lone pair to the metal but do not have additional metal-ligand interactions. The classic example is ammonia. The nitrogen in ammonia has only one lone pair to donate and is a simple sigma donor. Ethylenediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (en), is also a sigma donor because it has a single lone pair on each nitrogen atom. The en ligand is a slightly stronger sigma donor than ammonia. The difference is explained by the slightly stronger basicity of en compared to ammonia; the nitrogen lone pairs in en are better donors to both protons and metal ions.



The common pi donors include the halides and some oxygen donors. In these cases, the donor atom has an additional lone pair (or more) which may engage in formation of a pi bond by donation to a metal d orbital. Among the halides, fluoride produces the largest field splitting and iodide the smallest. This trend is also explained in terms of the relative basicity of these halides; fluoride is more basic than bromide. In addition, there is also understood to be better overlap between fluorine's p orbital and the d acceptor of a positively charged metal ion, compared to larger halides such as iodine.



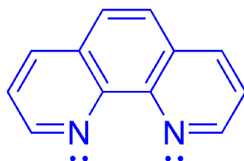
Oxygen donors do not follow this basicity trend. Hydroxide is thought to act as a better pi donor than water, partly because of its negative charge. A carboxylate ligand is not quite as strong a pi donor as hydroxide, probably because its lone pair is delocalized into the carbonyl group.



The pi acceptors include familiar examples such as carbon monoxide (carbonyl ligand) as well as the aromatic phenanthroline.



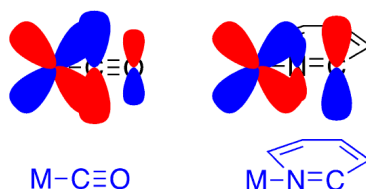
The phenanthroline may be an unfamiliar ligand. It is an aromatic amine, like pyridine. Other aromatic ligands, if they donate through a lone pair such as a phenyl, C_6H_5^- , can also be considered pi acceptors. These compounds feature a pi bond that includes the donor atom, so there is a π^* orbital at that position capable of undergoing back-donation from the metal.



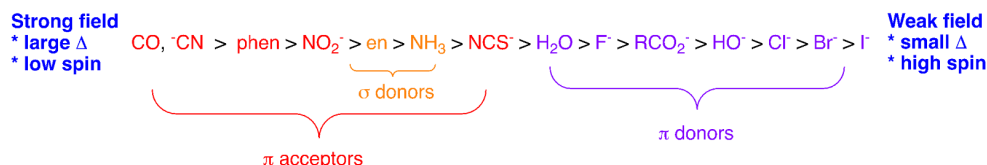
phenanthroline (phen)

Again, there are subtle variations among the field strengths exhibited by these pi acceptors, and there may be several factors contributing to those differences. For example, the cyanide is only slightly weaker field than the isoelectronic carbon monoxide. That small difference may be due to the negative charge on the cyanide rendering it a weaker electron acceptor. On the other hand, phenanthroline is neutral, but it is still a weaker donor than carbon monoxide. That weaker field may be due to the smaller lobe on the nitrogen atom in the π^* orbital in phenanthroline. Because nitrogen is more electronegative than carbon, it makes a greater contribution to the $\text{C}=\text{N}$ pi bonding orbital than carbon; the opposite is true in the antibonding orbital. Carbon monoxide, in contrast, features a larger lobe on carbon in its π^* orbital. The result is better metal-ligand pi overlap with carbon monoxide than with phenanthroline.

Phosphines are also commonly considered to be pi acceptors, for subtle reasons that have been subject to some debate.¹

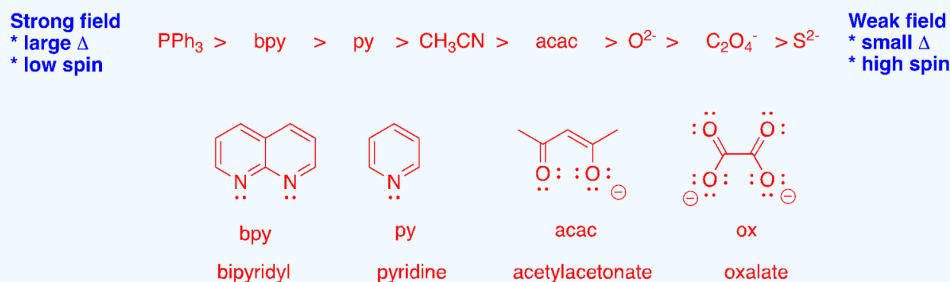


All three of these series can be collated to arrive at a combined list, which is a more complete spectrochemical series. Note that there may be some overlap between the different types of donors. Nevertheless, the overall trend holds: pi acceptors lead to the greatest field splitting on average, whereas di donors lead to the smallest.



✓ Example 8.4.2.1

Some additional common ligands are displayed according to field strength, below. Classify these ligands as pi donors, sigma donors, or pi acceptors.



Solution

PPh_3 , based on its structure, appears to be a sigma donor only because it has just one lone pair on the donor atom. However, phosphines tend to behave as pi acceptors; that is, they appear to withdraw some electron density from the metal as indicated by the response of reporter ligands such as CO.

Bpy, py and CH_3CN (acetonitrile) all appear to be pi acceptors. Like phen, they behave as weak pi acceptors.

Acac, oxide, oxalate and sulfide are all pi donors. The donor atom in each case has a lone pair in addition to the sigma donor pair.

References

1. Wolczanski, P. T. "Flipping the Oxidation State Formalism: Charge Distribution in Organometallic Complexes as Reported by Carbon Monoxide". *Organometallics* **2017**, 36, 622-631.

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