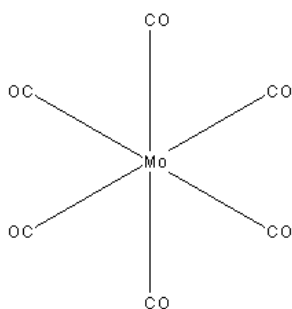
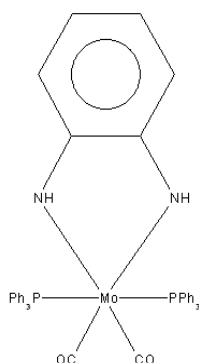


INTRODUCTION

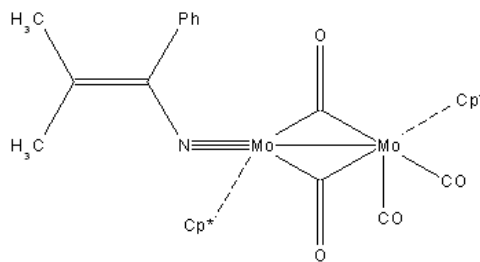
- Metal carbonyls are formed by complexation of a transition metal atom with carbon monoxide. In some cases carbon monoxide is the only ligand bound to the metal e.g. $\text{Mo}(\text{CO})_6$ (CSD reference code *FUBYIK*) but generally the metal carbonyl contains a mix of ligands e.g. $[\text{Mo}\{1,2\text{-(NH)}_2\text{C}_6\text{H}_4\}(\text{CO})_2(\text{PPh}_3)_2]$ (CSD reference code *PEPCES*).



FUBYIK



PEPCES



PALSOK

- The carbonyl ligand is versatile and can bond to the metal atom in a number of ways including in a bridging mode e.g. refcode *PALSOK*. However for the purposes of this example we are interested only in terminal carbonyls, the most common way in which carbonyls bind to metals.
- In metal carbonyls it is found that there is a complementary effect whereby the stronger (i.e. shorter) the MC bond, the weaker (i.e. longer) the corresponding CO bond.
- This effect is known as pi back-bonding.
- The effect of pi back-bonding can be nicely illustrated by performing a search of the Cambridge Structural Database while the explanation for why pi back-bonding occurs is explained by considering the molecular orbitals (specifically the HOMO (highest occupied molecular orbital) and LUMO (lowest occupied molecular orbital)) involved in the MCO bonding.

Use the < and > navigational buttons above to move between pages of the teaching module. Additional online resources can be accessed by clicking on the links on the right hand side of any page.

This module is divided into the following sections:

OBJECTIVES (see page 3)

GETTING STARTED (see page 3)

STEPS REQUIRED (see page 3)

ADVANCED EXERCISES (see page 10)

SUMMARY OF KEY CONCEPTS (see page 12)

OBJECTIVES

- To search for molybdenum carbon monoxide complexes in the CSD using ConQuest and monitor the MoC and CO bond lengths.
- To read the search results into Vista for further analysis.
- To rationalise the search results based on electron counting and orbital considerations.

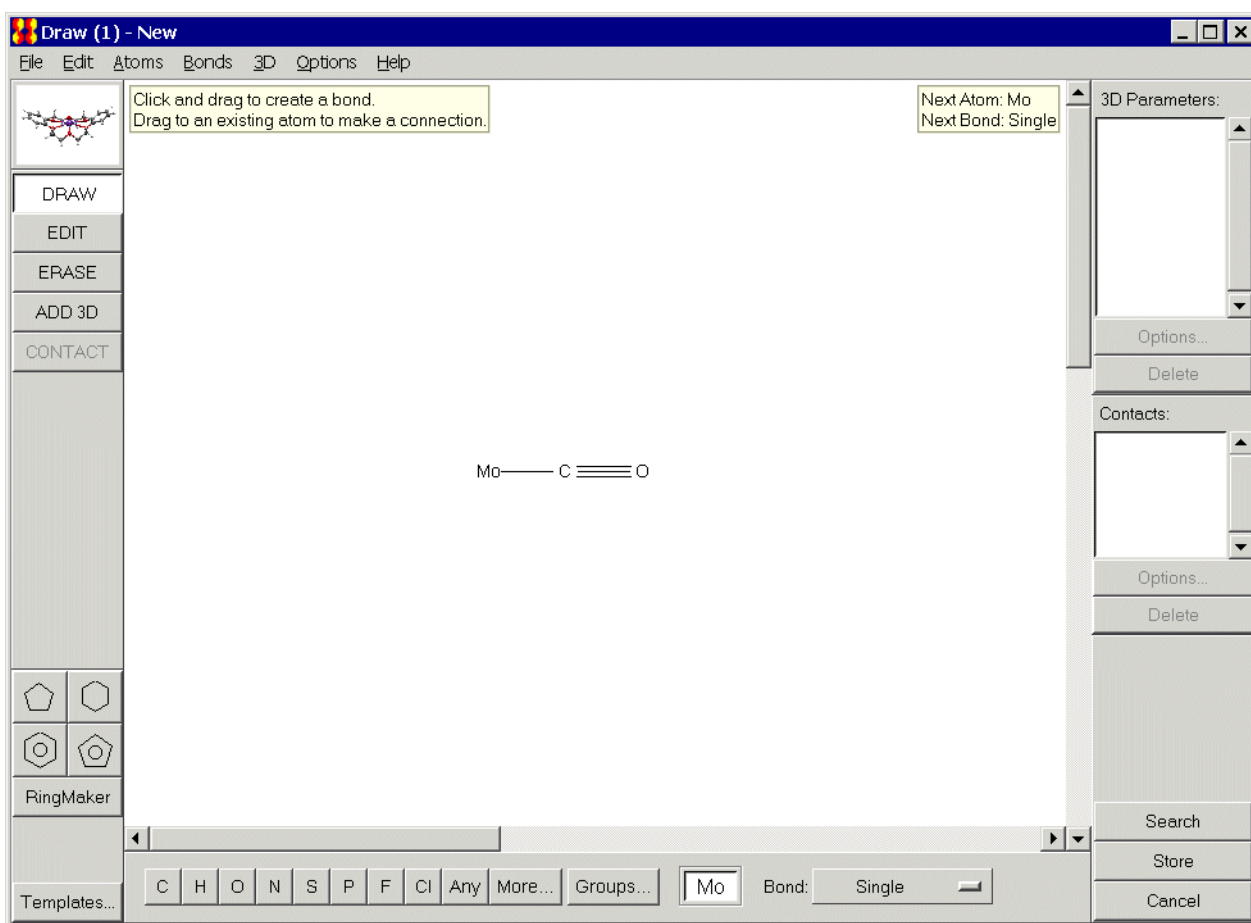
GETTING STARTED

- This module requires full access to the Cambridge Structural Database System. Specifically, the following software components will be used:
 - *ConQuest*, for search and retrieval of crystal structure data.
 - *Vista*, for analysis of geometric data retrieved using ConQuest.

1. STEPS REQUIRED

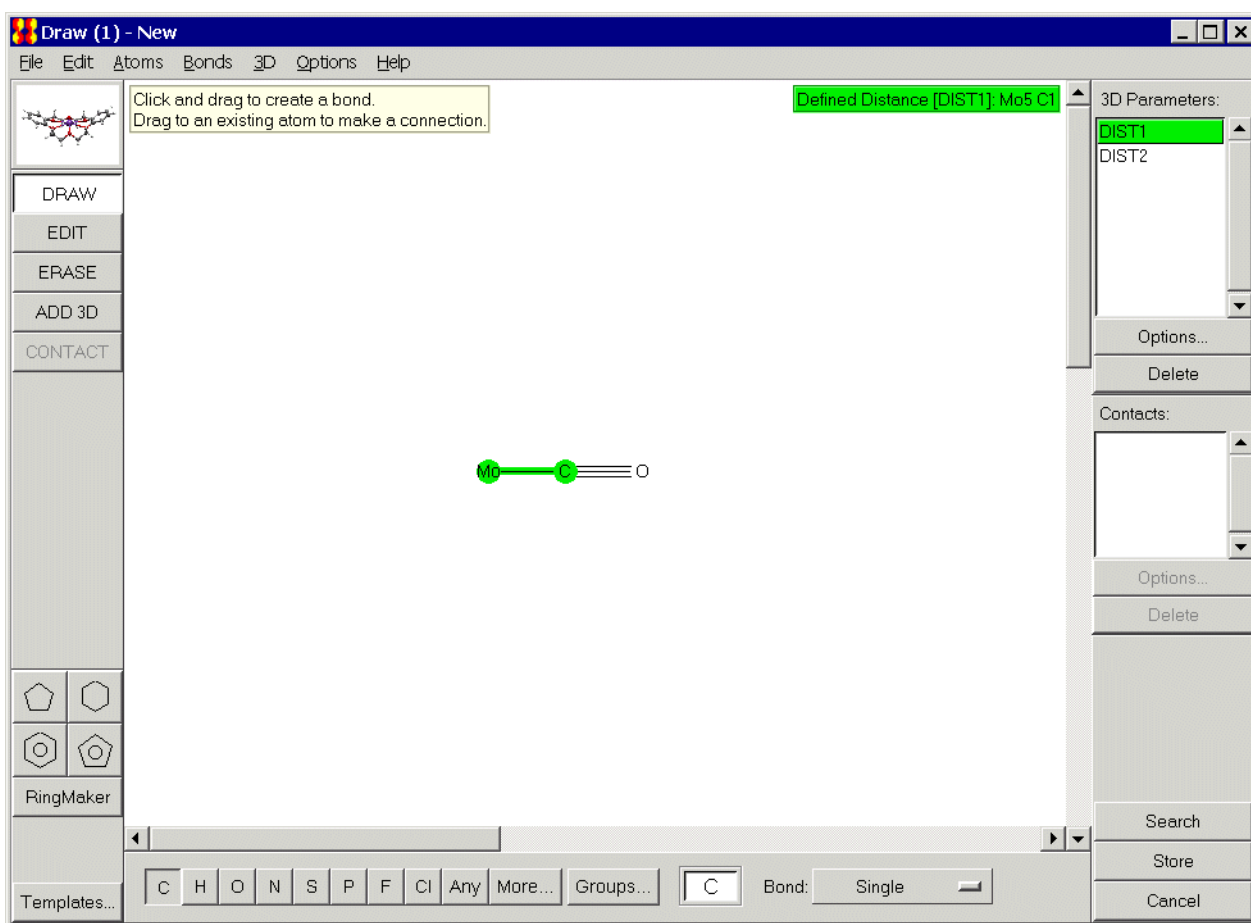
1.1 Define a search for molybdenum carbon monoxide complexes

- Start ConQuest and click on the **Draw** button on the left-hand side of the interface. This launches the sketcher window.
- The carbon **C** atom will be selected by default. Introduce a C atom into the sketcher window by left-clicking with the mouse in the middle of the window.
- We now need to draw an oxygen atom which is triply bonded to the C. In the atom list at the bottom of the sketcher, pick **O**, then move along to the **Bond:** pull down menu and select **Triple**. Go to the C atom in the sketcher. Left-click and keeping the left mouse button depressed, move the mouse to the right until you see a triple bond appear. Release the left mouse button, and an O atom will be drawn bonded to the C.
- Now bond a molybdenum atom to the C atom using a single bond by clicking on the **More** button at the bottom of the sketcher and selecting **Other Elements...** Pick **Mo** from the resultant periodic table, then click **OK**. Now change the bond style to **Single** using the *Bond:* pull down menu at the bottom of the sketcher window. Left-click on the C atom in the sketcher and keeping the mouse button depressed, move to the left until a single bond appears, at which point release the mouse button.
- The resultant substructure will look like the following:

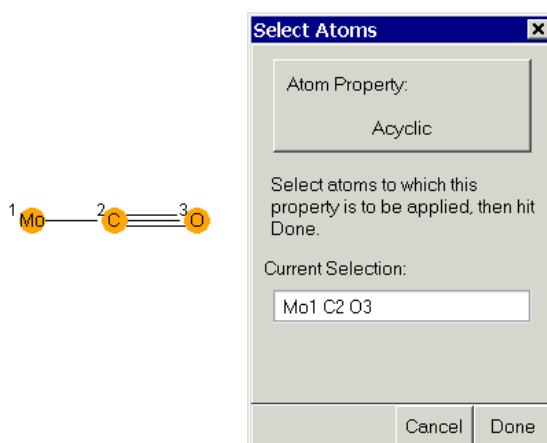


1.2 Define the relevant bond lengths of interest (the MoC and CO bonds) and apply some constraints

- Click on the **ADD3D** button on the top left of the sketcher. A pop-up window will appear. Click on the **Mo** then the **C** atom: they will be selected and you will notice the pop-up dialogue updates to reflect what is selected, i.e. you can now click on **Define** next to *Distance*. Now that this bond length has been defined it will be monitored during the ConQuest search of the Cambridge Structural Database.
- Define the CO bond in the same way, i.e. by selecting first the **C** atom then the **O** atom then by clicking **Define:** next to **Distance**.
- Once you have defined both bond lengths, you will notice they are both recorded in the top right of the sketcher window.



- Hit the **Done** button to close the *Geometric Parameters* window.
- We now need to restrict the cyclicity of all three atoms to specify that they do not belong to cyclic systems (e.g. cyclic ligands in the case of the CO) or organometallic networks.
- Go to the top level **Atoms** menu option and select **Cyclicity** from the resultant pull-down menu. We require the Mo, C and O atoms to be *Acyclic*, so select this from the menu. Now click on the Mo, C and O atoms, then hit the **Done** button to complete the definition.



- We now need to restrict the coordination numbers of the C and O atoms to ensure they are not bonded to any other atoms.
- Right-click on the C atom and pick **Number of Bonded Atoms**, then **2** from the resultant pull-down menus. This means that ConQuest will consider CSD entries where only the Mo and O atoms are bonded to the carbon.
- Now right-click on the O atom, but this time pick **1** from the *Number of Bonded Atoms* pull-down menu. This means that the O atom will form no bonds other than to the C atom.
- We also need to specify that the Mo atom is 6-coordinate. This is done in the same way as described above for C and O, i.e. right-click on the Mo atom then pick **Number of Bonded Atoms** then **6** from the resultant pull-down menus.

1.3 Set the search running and analyse the results

- Hit the **Search** button at the bottom of the sketcher window then hit **Start Search**.
- The search results (i.e. a list of CSD entries that contain a substructure that matches the one we've sketched) will be displayed in the *View Results* window. Scroll through the results list and inspect some of the hits. You will notice that some of the hits contain more than one occurrence of our defined fragment:

The screenshot shows the CCDC ConQuest software interface. The title bar reads "CCDC ConQuest (1) : search8 [Search]". The menu bar includes "File", "Edit", "Options", "View Databases", "Results", and "Help". The main window has tabs for "Build Queries", "Combine Queries", "Manage Hitlists", and "View Results".

On the left, there is a vertical menu with options: "Author/Journal", "Chemical", "Crystal", "Experimental", "Diagram" (highlighted in red), "3D Visualiser", "CSD Internals", and "Search Overview".

The central area displays the search results for Refcode: MUQBAB, CSD version 5.28 (November 2006). It shows a chemical structure of a molybdenum complex. The structure features a central ring with a methyl group (OMe) and a dimethylamino group (NMe₂). Two molybdenum (Mo) atoms are coordinated to the ring, each with three terminal carbonyl (CO) ligands. The Mo atoms are also coordinated to each other.

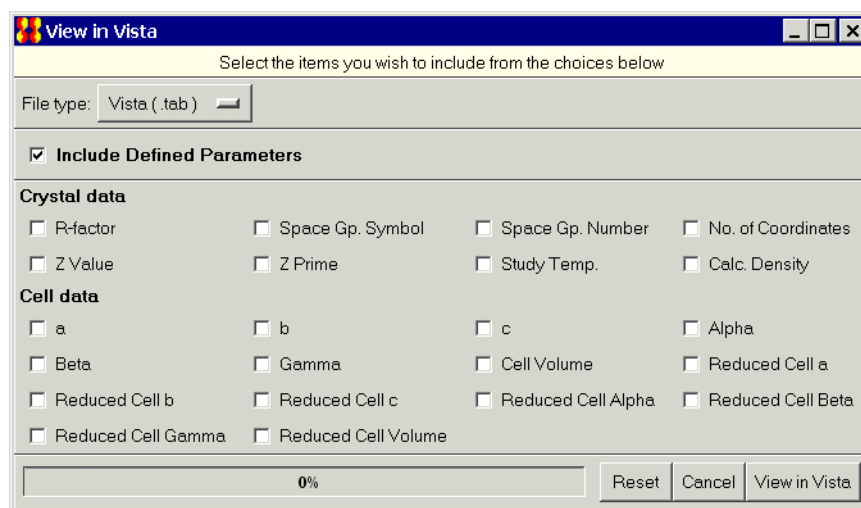
Parameters are listed on the right: DIST 1 (2,044) and DIST 2 (1,159).

At the bottom of the central area, there are controls for "Multiple Hits: Show 1 of 10" and "Show Parameters" (checked). Buttons for "Use as Query..." and "Detach Diagram" are also present.

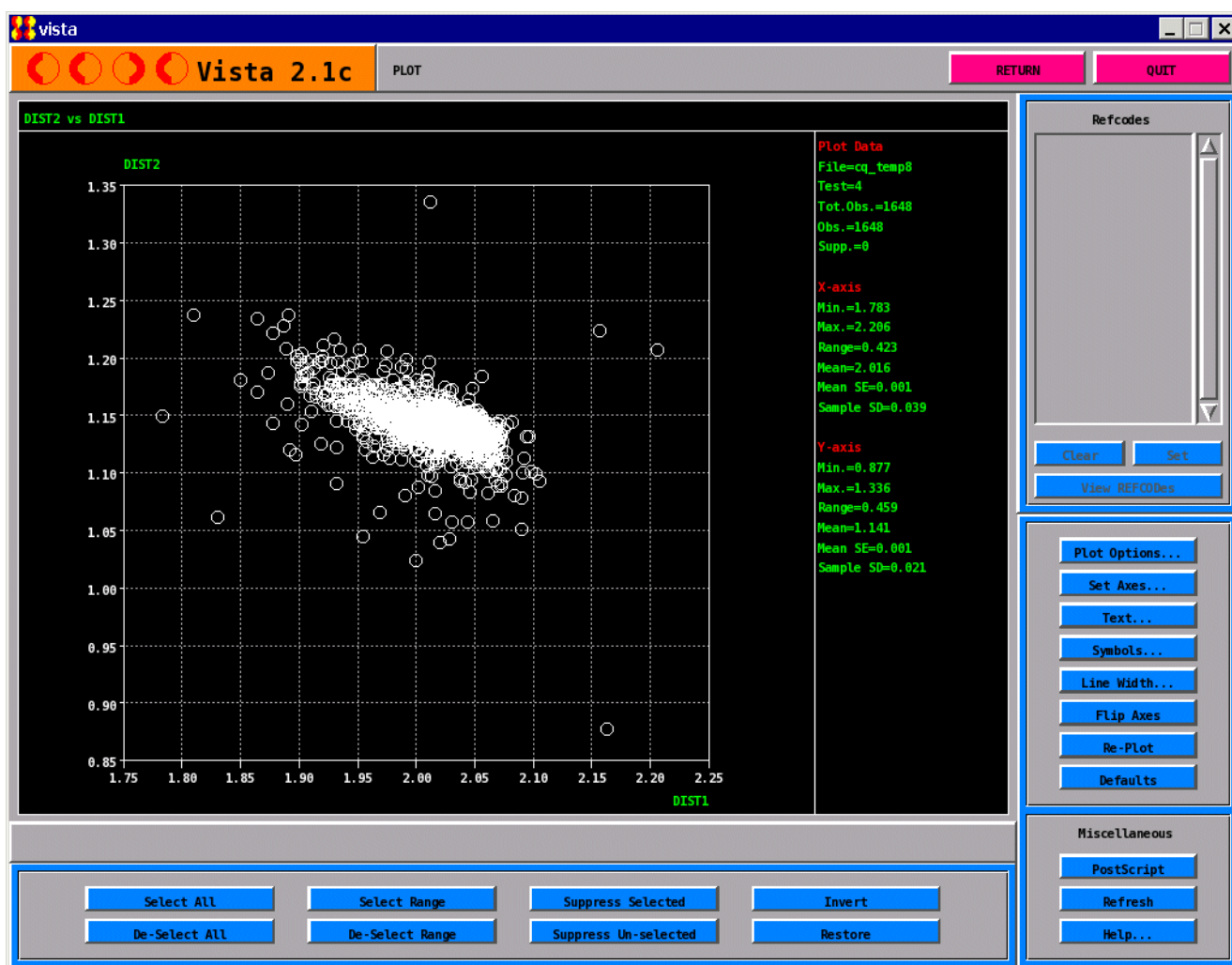
On the right side, there is a list of hits under the heading "Analyse Hitlist". The list includes: LAZTAI, LECZEY, LEMOID, LESWOV, LIBGIM, LIRHAV, LOOFEC, LOQYZ, LOQYOF, MAVDOC, MAVDUI, MILXIO, MIMYMO, MIZJIO, MIZJUA, MOJYT, MPGEMO, MUQBAB (highlighted in yellow), NAKTID, and MASDEC. Below the list, it shows "324 hits" and a "100%" progress bar. A "Stop Search" button is at the bottom right.

i.e. in the example above, *MUQBAB*, there are 10 MoCO substructure matches in the complex, each with different MoC and CO distances.

- We can scroll through each of the hits and view the values for the distances we've plotted individually, or alternatively we can read the search results into another software package for further analysis (e.g. Excel or Vista, the latter of which is distributed with the CSD System).
- Click on the **Analyse Hitlist** button at the top of the hitlist and pick **View in Vista**.



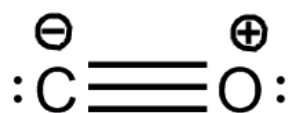
- We can import a number of parameters into Vista for inspection (e.g. Rfactor, a measure of the quality of the structure determination) however we're currently only interested in the parameters we've searched for, so hit the **View in Vista** button again.
- The Vista interface will display the search results, i.e. the two distances and the associated CSD refcode.
- Histograms (i.e. a plot of a geometric parameter versus its occurrence) or scattergrams (i.e. a plot of one parameter versus the other) can be plotted using Vista.
- Generate a scattergram of the MoC distance versus the CO distance. This is done by selecting the grey tabs at the top of the *DIST1* and *DIST2* columns, then by hitting the **Scattergram** button in the *Data Visualization* section of the interface.



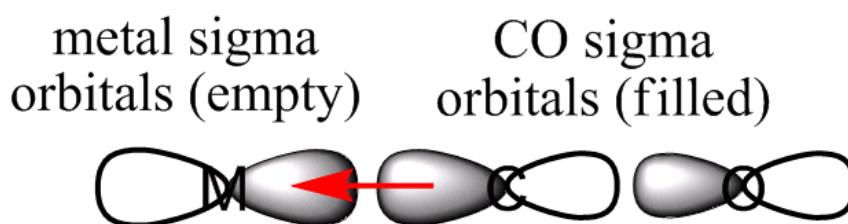
- If the scattergram is not in the orientation shown above, hit the **Flip Axes** button.
- What do you notice about the plot?
There is a linear relationship between the MoC and the CO distances.
- Plot a linear regression by hitting the **Plot Options** button, activating the **Linear regression** button, then hitting **OK**. This will make it apparent that as one distance increases, the other decreases.

1.4 Try and rationalise what you are seeing

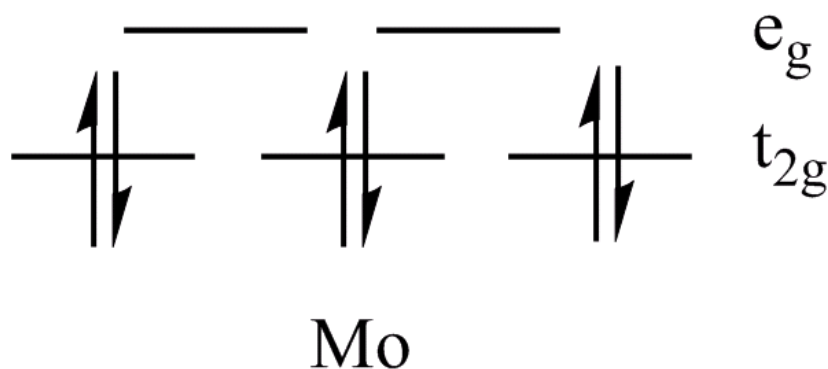
- Carry out an electron count on carbon monoxide, CO. It has 10 electrons, 6 of which are involved in bonding. The remaining 4 are divided between the C and the O atom, meaning the C atom has 2 electrons for metal bonding (note that the following is only one of the resonance forms of carbon monoxide).



- Thus the C is bonded to the Mo via a sigma bond; the lone pair on the C is donated to an empty metal sigma orbital:

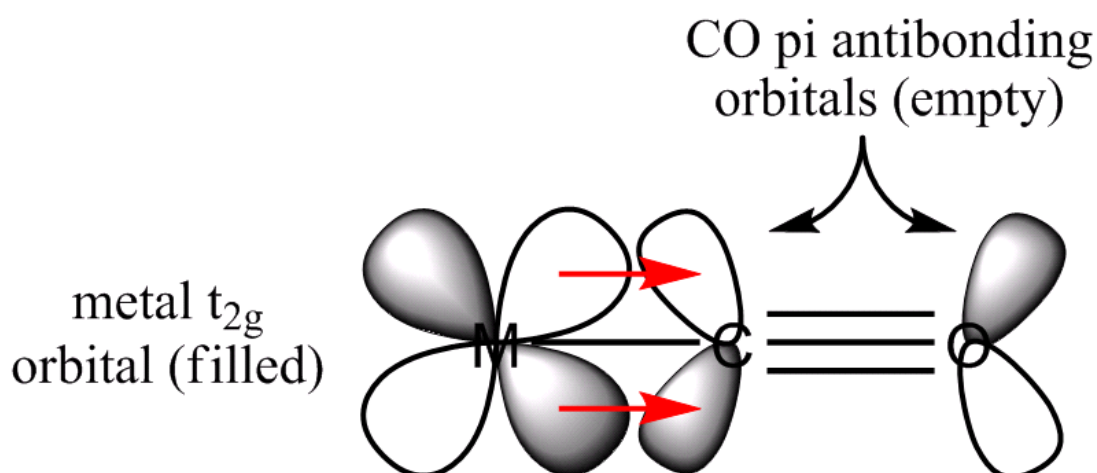


- There is a secondary bonding effect: the Mo atom is 6-coordinate and is d^6 , thus the orbital splitting diagram will resemble the following:



i.e. the t_{2g} orbitals are filled however the e_g orbitals are empty.

- The donation of electrons from the CO to the metal via the sigma bond effectively increases the electron density on the metal. The vacant carbon monoxide pi antibonding orbitals are of similar size to the filled metal t_{2g} orbitals, thus the additional electron density on the metal (arising from the MoC bond) is donated from the metal t_{2g} orbitals back to carbon antibonding orbitals as shown below.



- As the bonding is from the metal to the ligand rather than the usual ligand to metal, and because it involves pi orbitals, the phenomenon is termed ***pi back-bonding***. This effect occurs in all metals however the effect is observed more commonly in metals with at least d^4 electron configurations (fewer d electrons mean the metal has less electron density to donate back to the CO). We have used Mo in this example only to restrict the hitlist size.
- But how does this affect the MoC and CO distances?
- Donation of electrons from the CO to the Mo strengthens the MoC bond. But this effect increases the amount of electron density on the metal, which in turn means the metal has more electron density which it donates back to the CO. As the electron density involved in back-bonding is donated to the CO antibonding orbitals, this effectively lengthens the CO bond.
- Return to ConQuest and look at refcodes *DUSHAA* and *FOFTOK*.

	DUSHAA	FOFTOK
MoC distance	1.887Å	2.012Å
CO distance	1.228Å	1.140Å

- These structures are at opposing ends of the scattergram and illustrate the effect described above.

2. ADVANCED EXERCISES

2.1 What are the other resonance forms of CO?

- Only one of the resonance forms of CO was used above to describe how CO bonds to a metal. There are another two resonance forms: can you draw them?

SUMMARY OF KEY CONCEPTS

- Searching the CSD for molybdenum carbonyl complexes and monitoring the MoC and CO bonds illustrates there is an effect whereby as the MC bond distance lengthens, the corresponding CO bond distance shortens (and vice versa).
- The complementarity of this effect can be seen when the MoC distance is plotted against the CO distance in a statistical analysis package such as Vista: a linear relationship between the two distances is observed.
- This phenomenon is called pi back-bonding and can be explained by electron donation between bonding and anti-bonding orbitals.
- Pi back-bonding is found not only in MoCO complexes, but also other transition metal CO complexes.
- The strength of pi back bonding in a metal carbonyl complex can be monitored using IR spectroscopy.
- For optimal pi back bonding to occur, the metal must be in a low oxidation state.