

Question#44979 – Chemistry – Inorganic

Question:

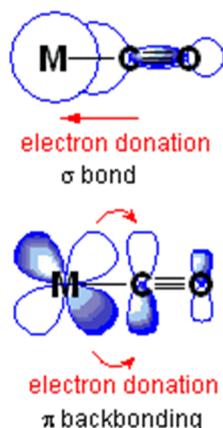
CO forms Lewis acid-base adduct with Ni^0 but not with Ni^{2+} . Why?

Answer:

To start with, a brief theory about bonding between Ni^0 and CO has to be mentioned.

Ni^0 forms nickel carbonyl compound $\text{Ni}(\text{CO})_4$. Pi-bonding occurs in this compound. The concept of pi-bonding (also called pi-backdonation) includes idea that electrons move from an atomic orbital on one atom to a π^* antibonding orbital on a π -acceptor ligand. Electrons from the metal are used for bonding with the ligand (CO in this case), in the process relieving the metal of excess negative charge.

A description of the bonding of π -conjugated ligands to a transition metal which involves a synergic process with donation of electrons from the filled π -orbital or lone electron pair orbital of the ligand into an empty orbital of the metal (donor-acceptor bond), together with release (back donation) of electrons from an nd orbital of the metal (which is of π -symmetry with respect to the metal-ligand axis) into the empty π^* -antibonding orbital of the ligand.



The scheme above represents CO's HOMO and LUMO orbitals (top). Middle part pictures sigma-electron donation from CO to metal's center (from CO's HOMO). Finally, the bottom sketch shows the contribution of π -donation from metal's d-orbitals to CO's LUMO.

Now let's consider what makes CO predominantly form compound with Ni^0 on the contrary to Ni^{2+} , which is not likely to interact with CO.

The postulated question about difference in bonding interaction between CO and nickel species can be solved in terms of HSAB theory. It assigns the terms 'hard' or 'soft', and 'acid' or 'base' to chemical species. 'Hard' applies to species which are small, have high charge numbers (the charge criterion applies mainly to acids, to a lesser extent to bases), and are weakly polarizable. 'Soft' applies to species which are big, have low charge states and are strongly polarizable. The main part of this theory is that soft acids react easily and form stronger bonds with soft bases, at the same time hard acids are more related with hard bases, all other factors being equal. Ni^0 and CO are both soft acid and base, which can explain what makes them related and more eager to form compound. As soft species, they have several common properties:

- large atomic/ionic radius
- low or zero oxidation number
- high polarizability
- low electronegativity

On the contrary, Ni^{2+} can't be defined as soft acid. According to its properties, it is rather somewhere between hard and soft acids. Such acids are called borderline acids. Thus they tend to have lower charge and larger size than hard acids, and higher charge and smaller size than soft acids.

To summarize, Ni^0 is more likely to form acid-base adduct with CO than Ni^{2+} because Ni^0 and CO are more related due to their soft-acidic nature.