The Transition Metal Enigma: A Study of Oxidation States

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Purpose:
To find a non-ambiguous method of determining the oxidation state (OS) of transition metals (TM) within complexes and create new models for transition metal chemistry. By using density functional theory (DFT) calculations, theoretical values will be correlated to verify "experimentally" determined oxidation states and extrapolated to novel complexes.

How OS Applies to Human Biology:

Conclusions:
In complexes without \( \pi \)-backdonation, occupied orbitals are clearly defined, allowing a facile OS determination. With a facile route to determine the OS of TM complexes, more reactions can now be studied from calculations, theoretical values will be correlated to a multifaceted perspective rather than a dissociation between experimental and theoretical results.

Pitfalls:
While the OS method is effective in most cases, caution must be exerted. For the carbonyl complexes, as well other cases where extensive \( \pi \)-backdonation occurs, the method is more ambiguous. As shown in Table 1, \( \text{Cr(CO)}_6 \) has occupation numbers below the anticipated values. This occurs due to the metal donating its electrons into unfilled anti-bonding orbitals as shown in Figure 3. In this case, two forces are competing for stability. Filling the anti-bonding orbital decreases stability, but the metal is donating electrons increasing the overall stability. Such instances elude a chemist’s intuition and must be carefully analyzed.

Some Complexes of Interest:

Future Work:
An in-depth study of bonding interactions within several carbonyls of various geometries as well as the nitrogen counter part nitrosyl (NO).

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Method:

• Using the Gaussian09 suite of programs, calculations were performed using spin-unrestricted density functional theory. The SCF convergence criteria was tightened to \( 1 \times 10^{-6} \) using IOP(4/28=9). All other criteria were default. The B3LYP exchange-correlation functional was used for each complex and the Stuttgart-Dresden (SDD) basis set / effective core potential (ECP) basis was used on all metal atoms. On non-metal atoms the Pople-style 6-31G(d) basis set was used.

• Natural Bond Orbital (NBO) analyses were then performed using the NBO 5.0 suite. The \( 5 \times 5 \) matrix was removed and diagonalized to find the eigenvalues of the system (these eigenvalues correspond to the electron occupancy i.e. 1.00=1e). The unusually low occupation numbers in the table occur from \( \pi \)-backdonation to the carbonyl.

Data:

Ex.

A simplified definition of OS refers to the number of electrons on atom.

<table>
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<th>Method:</th>
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Data:

| Table 1: Occupation numbers correspond to number of electrons (i.e. 1.00 = 1e). Bolded numbers are considered occupied even though they may not be equal to 1.00. |

Figure 3

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