

Exercise 3. Coordination, symmetry and synergy

Reading material

- F. M. Bickelhaupt, U. Radius, A. W. Ehlers, R. Hoffmann, E. J. Baerends, *New J. Chem.* **1998**, 22, 1.
- Diefenbach, F. M. Bickelhaupt, G. Frenking, *J. Am. Chem. Soc.* **2000**, 122, 6449.
- M. G. Goesten, C. Fonseca Guerra, F. Kapteijn, J. Gascon, F. M. Bickelhaupt, *Angew. Chem. Int. Ed.* **2015**, 54, 12034.

Introduction

In this exercise, you will study the metal-ligand bonds in $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$. The analyses will be done by two different fragment approaches, namely

1. with ML_{n-1} as fragment 1 and L as fragment 2;
2. with M as fragment 1 and L_6 (the ligand cage) as fragment 2.

The purpose of this exercise is to obtain a complete picture of the interaction mechanism of each coordination complex. The analyses will be carried out within the framework of Kohn-Sham MO theory, in combination with a quantitative energy decomposition analysis (EDA) and Voronoi deformation density (VDD) analysis.

Step 1. Optimize structures and compute ΔE

Optimize the structures at the BLYP/TZ2P level of theory, and compute the electronic bond energy ΔE in terms of both fragment approaches (make sure you understand the physical meaning of each approach). Analyze the M-C and C-O bond lengths. Is there a correlation between the M-C and C-O bond lengths and the electronic bond energy ΔE ?

Technical notes

Use the correct symmetry point group for each optimization. It will then be possible to decompose the orbital interaction term into contributions from each irreducible representation, which will provide you with valuable information about the interaction mechanisms.

In approach 2, you should compute the energy of the ligand cage in frozen geometry. Note that this will give the instantaneous interaction energy ΔE_{int} between the metal and ligand cage.

Step 2. EDA and KS-MO analysis

Perform an EDA on each complex with fragment approach 1 and 2. What are the contributions of ΔE_{strain} , ΔV_{elstat} , ΔE_{Pauli} and ΔE_{oi} to the M-CO bond strength, and do they follow the same trend as ΔE_{int} ? How important are the σ and π contributions?

Perform KS-MO analyses to rationalize the outcomes in ΔE_{oi} . Which orbitals are the most important for the σ interaction? And which ones for the π interaction? Analyze the charge flow by considering the gross populations and the VDD atomic charges. Can you explain the differences in ΔE_{int} and ΔE_{oi} based on your MO analyses? Take into account the orbital energies and orbital overlap.

Technical notes

*Each point group consists of a number of irreducible representations. You can determine whether they are associated with σ - or π type interactions by visualizing the orbitals. For a schematic representation of this principle, see for example J. Am. Chem. Soc. **2000**, 122, 6449.*

Step 3. Synergy between σ and π

In the next step, you will consider if there is a so-called cooperative reinforcement between the σ and π charge transfer interactions. This is done by computing the difference between $\Delta E_{\text{oi}}(\sigma, \pi; \sigma, \pi)$, in which σ and π charge transfer occur simultaneously, and the individual $\Delta E_{\text{oi}}(\sigma, -; \sigma, -)$ and $\Delta E_{\text{oi}}(-, \pi; -, \pi)$ interactions, in which there is only σ or π charge transfer, respectively:

$$\Delta E_{\text{syn}} = \Delta E_{\text{oi}}(\sigma, \pi; \sigma, \pi) - \Delta E_{\text{oi}}(\sigma, -; \sigma, -) - \Delta E_{\text{oi}}(-, \pi; -, \pi) \quad (1)$$

A negative value of the synergy ΔE_{syn} corresponds to a stabilizing cooperative effect, and a positive value corresponds to a destabilizing cooperative effect. The individual $\Delta E_{\text{oi}}(\sigma, -; \sigma, -)$ and $\Delta E_{\text{oi}}(-, \pi; -, \pi)$ can be computed by switching of the σ or π virtual orbitals of the interacting monomers. An example of such a computation is given in the appendix.

Compute ΔE_{syn} for each complex in terms of fragment approach 1 and 2. Is there a cooperative reinforcement? Explain your findings.

Step 4 (optional). Additional ligands

If there is still time left: analyze $\text{ML}_5\text{L}'$ with $\text{L}' = \text{CO}$, N_2 , BF , SiO , NH_3 and PH_3 in terms of fragment approach 1 (so, the interaction between ML_5 and L'). Analyze the electronic structure of each ligand, and rationalize whether they will have good metal binding abilities. Verify your

reasoning by computing ΔE and performing an EDA. Are the outcomes in line with what you expected?

Step 5 (optional). Additional transition metals

If there is still some time left: analyze $M(\text{CO})_6^q$ with $M^q = \text{Hf}^{2-}, \text{Ta}^-, \text{W}, \text{Re}^+, \text{Os}^{2+}$ and Ir^{3+} in terms of fragment approach 1 and 2. Optimize the structures, compute ΔE and perform an EDA. Answer the same questions as in Step 2. How are the outcomes influenced by the charge on the metal? Can you explain your observations?

Step 6 (optional). Influence d orbitals

Verify the study that was published in *Angew. Chem. Int. Ed.* **2015**, 54, 12034. In this work, the bonding in six-coordinate complexes $M(\text{H}_2\text{O})_6$ has been studied with Group 13 elements (no d orbitals) and transition metals (d orbitals present). What is the difference between the metal-ligand bonds with and without d orbitals?

Appendix. Removing virtual orbitals

To compute the synergy ΔE_{syn} , you need to inhibit the charge transfer in the σ and π system, respectively. This can be done by “switching off” all σ or all π virtual orbitals of the interacting monomers. The easiest way to do this is as follows. Simply do the single point computations as you would normally do for a fragment analysis. In the actual fragment analysis input file, you should specify the number of virtual orbitals that you want to remove from each irreducible representation. For example, if you want to switch off all virtual σ interactions in a complex with C_s symmetry to obtain $\Delta E_{\text{oi}}(-, \pi; -, \pi)$, you would add the following lines to your input file:

```
FRAGMENTS
1 $SLURM_SUBMIT_DIR/1.t21
2 $SLURM_SUBMIT_DIR/2.t21
END
```

REMOVEFRAGORBITALS

```
1
  AA 20
SUBEND

2
  AA 20
SUBEND
END
```

where AA refers to the irreducible representation that is associated with σ interactions, and 20 is the number of virtual orbitals that will be removed. The total number of virtual orbitals can be obtained by opening the output file of the single point files of each fragment. Look up the total number of SFO's per irrep (found under *SFOs*), and subtract the number of occupied orbitals. Make sure you use no frozen core. You can verify if you removed the correct number of virtual orbitals by opening the .t21 fragment analysis file in adflevels; no virtual orbitals of the irrep of choice should be present.