

Supporting Information

Electrochemical behaviors and relativistic DFT calculations to understand the terminal ligand influence on the $[\text{Re}_6(\mu_3\text{-Q})_8\text{X}_6]^{4-}$ Clusters

Macarena Rojas-Poblete^{a,e}, Alexander Carreño^{a,b}, Manuel Gacitúa^c, Dayán Páez-Hernández^{a,b,*},
Walter A. Rabanal-León^d, and Ramiro Arratia-Pérez^{a,b*}

a. Center of Applied Nanosciences (CANS), Universidad Andrés Bello, República 275, Santiago, Chile.

b. Núcleo Milenio de Ingeniería Molecular para Catálisis y Biosensores (MECB), ICM, Chile.

c. Facultad de Química y Biología, USACH, Av. L.B. O'Higgins 3363, Santiago, 7254758, Chile.

d. Departamento de Ciencias Químicas, Facultad Ciencias Exactas, Universidad Andrés Bello, Av. República 498, Santiago, Chile.

e. Universidad Tecnológica de Chile INACAP, Chile

*Corresponding author.

| Contents | Page |
|----------|------|
|----------|------|

| | |
|--|----|
| 1. Description of the methods used to calculate free energies. | S1 |
|--|----|

| | |
|---|----|
| 2. Table 1: Calculated Values of Changes in Gibbs Free Energies (kcal/mol) and Ground-State Redox Potentials (Volts) of the Rhenium-Sulfur Complexes Using SC-ZORA/BP86/TZ2P. | S2 |
|---|----|

| | |
|--|----|
| Table 2: Calculated Values of Changes in Gibbs Free Energies (kcal/mol) and Ground-State Redox Potentials (Volts) of the Rhenium-Selenium Complexes Using SC-ZORA/BP86/TZ2P. | S3 |
|--|----|

1. Description of the methods used to calculate free energies.

Using the following equation

$$\Delta G_s^0(\text{redox, soln}) = \Delta G_s^0(\text{redox, gas}) + \Delta G_s^0(\text{ox}) - \Delta G_s^0(\text{red}) \quad (1)$$

Where 0 denotes a standard state of 1 mol/L, G is the Gibbs free energy for oxidized cluster ($\Delta G_s^0(\text{ox})$) and reduced cluster ($\Delta G_s^0(\text{red})$).

$$\Delta G_s^0 = H_s^0 - TS_s^0 \quad (\text{ox}) \quad (2)$$

$$\Delta G_s^0 = H_s^0 - TS_s^0 \quad (\text{red}) \quad (3)$$

Where H is the enthalpy (kcal atmL/ mol), T the temperature (Kelvin) and S the entropy (kcal / molK) we have

$$H_s^0 = U_s^0 + (PV)_s^0 \quad (\text{ox}) \quad (4)$$

$$H_s^0 = U_s^0 + (PV)_s^0 \quad (\text{red}) \quad (5)$$

With U equal to the internal energy (kcal /mol), P pressure (atm) and volume V (liters) then you can get

$$G_s^0 = U_s^0 + (pV)_s^0 - TS_s^0 \quad (\text{ox}) \quad (6)$$

$$G_s^0 = U_s^0 + (pV)_s^0 - TS_s^0 \quad (\text{red}) \quad (7)$$

Uniting both equations

$$\Delta G_s^0(\text{redox, gas}) = U_s^0(\text{red}) - U_s^0(\text{ox}) - T(S_s^0(\text{red}) - S_s^0(\text{ox})) \quad (8)$$

$$\Delta G_s^0(\text{redox, gas}) = \Delta U - T\Delta S \quad (9)$$

Once $\Delta G_s^0(\text{redox, soln})$ calculated, can be estimated potential relative oxidation, E^0 , defined by:

$$E^0 = - \Delta G_s^0(\text{redox, soln})/nF \quad (10)$$

Where n is the number of electrons consumed or generated in the half-reaction of interest, and F is the Faraday constant. The potential is expressed in volt units (for free energy expressed in some typical units, $F = 23.061$ kcal per volt gram-equivalent).

2. Table 1: Calculated Values of Changes in Gibbs Free Energies (kcal/mol) and Ground-State Redox Potentials (Volts) of the Rhenium-Sulfur Complexes Using SC-ZORA/BP86/TZ2P.

| Complexes | Gas-phase G (kcal/mol) | Solv-phase G (kcal/mol) | ΔG (gas) | ΔG^n (solv) | ΔG^0 (solv) | $\Delta G^*(\text{soln})$ | $E^*(\text{abs})$ V | $E^*(\text{SHE})$ V |
|--|------------------------|-------------------------|------------------|---------------------|---------------------|---------------------------|---------------------|---------------------|
| $[\text{Re}_6\text{S}_8\text{F}_6]^{4-}$ | -3034.34 | -3522.54 | -169.89 | -488.19 | -553.50 | -104.58 | 4.53 | 0.35 |
| $[\text{Re}_6\text{S}_8\text{F}_6]^{3-}$ | -2864.46 | -3417.96 | | | | | | |
| $[\text{Re}_6\text{S}_8\text{Cl}_6]^{4-}$ | -2849.47 | -3295.58 | -183.83 | -446.12 | -521.91 | -108.04 | 4.68 | 0.50 |
| $[\text{Re}_6\text{S}_8\text{Cl}_6]^{3-}$ | -2665.64 | -3187.55 | | | | | | |
| $[\text{Re}_6\text{S}_8\text{Br}_6]^{4-}$ | -2803.10 | -3229.06 | -189.89 | -425.96 | -506.94 | -108.91 | 4.72 | 0.53 |
| $[\text{Re}_6\text{S}_8\text{Br}_6]^{3-}$ | -2613.21 | -3120.15 | | | | | | |
| $[\text{Re}_6\text{S}_8\text{I}_6]^{4-}$ | -2730.99 | -3140.93 | -209.38 | -409.94 | -512.92 | -106.39 | 4.61 | 0.43 |
| $[\text{Re}_6\text{S}_8\text{I}_6]^{3-}$ | -2521.62 | -3034.53 | | | | | | |
| $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$ | -4696.53 | -5174.35 | -173.18 | -477.82 | -536.52 | -114.47 | 4.96 | 0.78 |
| $[\text{Re}_6\text{S}_8(\text{CN})_6]^{3-}$ | -4523.35 | -5059.87 | | | | | | |
| $[\text{Re}_6\text{S}_8(\text{NC})_6]^{4-}$ | -4646.01 | -5094.14 | -177.79 | -448.12 | -511.69 | -114.22 | 4.95 | 0.77 |
| $[\text{Re}_6\text{S}_8(\text{NC})_6]^{3-}$ | -4468.22 | -4979.92 | | | | | | |
| $[\text{Re}_6\text{S}_8(\text{NCO})_6]^{4-}$ | -5654.02 | -6192.63 | -148.86 | -538.60 | -578.36 | -109.10 | 4.73 | 0.54 |
| $[\text{Re}_6\text{S}_8(\text{NCO})_6]^{3-}$ | -5505.16 | -6083.52 | | | | | | |
| $[\text{Re}_6\text{S}_8(\text{NCS})_6]^{4-}$ | -5257.01 | -5761.25 | -170.85 | -504.25 | -561.63 | -113.47 | 4.92 | 0.73 |
| $[\text{Re}_6\text{S}_8(\text{NCS})_6]^{3-}$ | -5086.16 | -5647.79 | | | | | | |
| $[\text{Re}_6\text{S}_8(\text{OCN})_6]^{4-}$ | -5597.73 | -6079.67 | -175.51 | -481.94 | -536.55 | -120.90 | 5.24 | 1.05 |
| $[\text{Re}_6\text{S}_8(\text{OCN})_6]^{3-}$ | -5422.22 | -5958.77 | | | | | | |

The redox potentials were corrected to $E^0(\text{SHE}) = 4.188\text{V}$

The experimental ΔG^0 values were calculated from the absolute redox potentials (4.188V was added to the redox potentials listed in the table).

*absolute value

3. Table 2: Calculated Values of Changes in Gibbs Free Energies (kcal/mol) and Ground-State Redox Potentials (Volts) of the Rhenium-Selenium Complexes Using SC-ZORA/BP86/TZ2P.

| Complexes | Gas-phase G (kcal/mol) | Solv-phase G (kcal/mol) | ΔG (gas) | ΔG^n (solv) | ΔG^o (solv) | $\Delta G^*(\text{soln})$ | E^* (abs) V | $E^*(\text{SHE})$ V |
|---|------------------------|-------------------------|------------------|---------------------|---------------------|---------------------------|---------------|---------------------|
| $[\text{Re}_6\text{Se}_8\text{F}_6]^{4+}$ | -2908.05 | -3392.95 | -170.60 | -484.90 | -552.05 | -103.44 | 4.49 | 0.30 |
| $[\text{Re}_6\text{Se}_8\text{F}_6]^{3-}$ | -2737.45 | -3289.51 | | | | | | |
| $[\text{Re}_6\text{Se}_8\text{Cl}_6]^{4+}$ | -2722.28 | -3163.49 | -180.62 | -441.21 | -517.92 | -103.90 | 4.51 | 0.32 |
| $[\text{Re}_6\text{Se}_8\text{Cl}_6]^{3-}$ | -2541.66 | -3059.58 | | | | | | |
| $[\text{Re}_6\text{Se}_8\text{Br}_6]^{4+}$ | -2677.77 | -3098.42 | -186.15 | -420.65 | -502.30 | -104.49 | 4.53 | 0.34 |
| $[\text{Re}_6\text{Se}_8\text{Br}_6]^{3-}$ | -2491.63 | -2993.93 | | | | | | |
| $[\text{Re}_6\text{Se}_8\text{I}_6]^{4+}$ | -2610.65 | -3011.19 | -208.03 | -400.54 | -505.48 | -103.10 | 4.47 | 0.28 |
| $[\text{Re}_6\text{Se}_8\text{I}_6]^{3-}$ | -2402.61 | -2908.09 | | | | | | |
| $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4+}$ | -4582.52 | -5059.63 | -169.74 | -477.11 | -536.36 | -110.49 | 4.79 | 0.60 |
| $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{3-}$ | -4412.78 | -4949.14 | | | | | | |
| $[\text{Re}_6\text{Se}_8(\text{NC})_6]^{4+}$ | -4524.50 | -4969.24 | -174.25 | -444.74 | -509.31 | -109.68 | 4.76 | 0.57 |
| $[\text{Re}_6\text{Se}_8(\text{NC})_6]^{3-}$ | -4350.24 | -4859.56 | | | | | | |
| $[\text{Re}_6\text{Se}_8(\text{NCO})_6]^{4+}$ | -5534.34 | -6065.64 | -143.18 | -531.29 | -568.91 | -105.56 | 4.58 | 0.39 |
| $[\text{Re}_6\text{Se}_8(\text{NCO})_6]^{3-}$ | -5391.17 | -5960.08 | | | | | | |
| $[\text{Re}_6\text{Se}_8(\text{NCS})_6]^{4+}$ | -5136.79 | -5634.49 | -164.81 | -497.70 | -556.61 | -105.90 | 4.59 | 0.40 |
| $[\text{Re}_6\text{Se}_8(\text{NCS})_6]^{3-}$ | -4971.98 | -5528.59 | | | | | | |
| $[\text{Re}_6\text{Se}_8(\text{OCN})_6]^{4+}$ | -5470.89 | -5946.62 | -172.18 | -475.74 | -533.08 | -114.84 | 4.98 | 0.79 |
| $[\text{Re}_6\text{Se}_8(\text{OCN})_6]^{3-}$ | -5298.70 | -5831.78 | | | | | | |

The redox potentials were corrected to $E^0(\text{SHE}) = 4.188\text{V}$

The experimental ΔG^0 values were calculated from the absolute redox potentials (4.188V was added to the redox potentials listed in the table).

*absolute value