



Investigation of Heavy Metal Adsorption to Hydrothermal Char

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Abstract

Sustainable solutions to remove heavy metal contaminants from the water supply are of critical importance to human health and the environment. This project investigates the use of hydrothermal char, a carbonaceous product of hydrothermal carbonization, as a heavy metal cation adsorbent. In this work, simulations based on density functional theory (DFT) are used to evaluate the adsorption of copper and lead to a proposed hydrothermal char molecule. It is shown that adsorption sites containing acidic hydrogens are most favorable. It is also shown that surface charge density, Born energy, and electric potential energy are strongly correlated to the computationally determined potassium exchange energy. A methodology for the experimental validation of the proposed approach is also provided.

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Introduction

Environmental heavy metal contamination poses a serious threat to both human health and the environment. The term “heavy metal” refers to metals with molecular weights higher than that of water; several examples are cadmium, chromium, nickel, lead, copper, zinc, and mercury (Gupta, 2021). Heavy metal contamination has existed for thousands of years – the Romans, for example, used lead piping in aqueducts which contributed to widespread lead poisoning. Today, over 2 billion people do not have access to safely managed drinking water, putting them at risk for heavy metal poisoning (Osseiran and Lufadeju, 2019).

The agricultural, industrial, and urban sectors contribute heavily to heavy metal contamination. Heavy metals in urban runoff, industrial wastewater, and sewage effluents contribute to water contamination. Furthermore, industrial processes can release heavy metals into the atmosphere, which ultimately are deposited into the soil and waterways. The usage of heavy-metal-containing pesticides and fertilizers, both for agricultural and domestic purposes, is also a significant source of soil and water contamination (Srivastava, 2017).

Heavy metals damage the environments they are deposited into, culling off non-resistant vegetation and imparting deadly health effects on animals. Two of the most abundant contaminants originating from industrial effluents are copper and lead (Ren et al., 2012). Copper contamination arises from a plethora of sources, including the electroplating, paper, pulp, steelmaking, metallurgy, chemical, circuit board, and paint industries, in addition to fertilizers. Copper poisoning can cause symptoms such as hair loss and kidney damage (Gupta, 2021), as well as liver damage (Briffa, 2020). Lead contamination is largely attributed to lead-acid batteries, as well as the electroplating, electrical manufacturing, steel, and explosives industries (Gupta, 2021). Lead poisoning causes profound damage to human health, including birth defects (Briffa, 2020), kidney and nervous system damage, and cancer (Gupta, 2021).

As heavy metals are nonbiodegradable, environmental accumulation is a growing issue that will continue damaging the environment and endangering human health until decontamination measures are taken. Heavy metal contamination in water supplies is particularly pertinent as it poses a direct threat to human health from drinking water, and this risk is exacerbated in developing countries. Finding a sustainable solution to remove heavy metals from waterways is therefore of utmost importance and can benefit the lives of many.

Recent work by Delahaye et al. (2020) has shown that natively available substances, such as glucose, can be processed with hydrothermal carbonization to provide an adsorbent for heavy metals. This work showed the promise of hydrothermal char as a tool to reduce heavy metal contamination in water supplies, but there is a key knowledge gap regarding the disparities in adsorption capacities of different metals. The objective of this research was to use density functional theory (DFT) to computationally assess the adsorption of copper (II) and lead (II) to hydrothermal char, as well as to assess whether DFT can be used to predict the adsorption trends of different metals to a hydrothermal char molecule.

Background

Heavy Metal Decontamination Strategies

There has been much research into possible strategies to remove heavy metal contamination from water supplies. Strategies include chemical precipitation, sedimentation and flocculation, flotation, ion exchange, adsorption, and membrane processes (Bilal et al, 2021; Delahaye et al., 2020). However, these strategies are limited in practical application due to constraints, such as low capacity, inefficiency at lower concentrations, high operation cost, and weak selectivity. More recently, decontamination strategies involving adsorption have gained attraction due to their ease of operation, regeneration and reusability, lower cost, efficiency at varied pH levels, and capacity to remove complex forms of metals in comparison to other techniques (Bilal et al., 2021).

Adsorption

Adsorption is the process through which particles are transferred from a bulk solution to a surface (Artioli, 2008). The chemical being adsorbed is known as the adsorbate, and the chemical providing the surface for adsorption is known as the adsorbent. Adsorption can be categorized as physical or chemical adsorption (Artioli, 2008). Despite the binary nomenclature, it is often the case that adsorption is due to both physical and chemical forces (Hu and Xu, 2020).

Physical and Chemical Adsorption

Physical adsorption is caused by Van der Waals forces. Physical adsorption is considered nonspecific due to the ubiquity of the Van der Waals force between substances. Additionally, because physical adsorption does not require a chemical reaction, it has a small adsorption energy. Because Van der Waals forces are weak, physically adsorbed substances can dissociate from the adsorbent with relative ease (Gupta et al., 2021; Hu and Xu, 2020).

Chemical adsorption is caused by the formation of a chemical bond. It is considered specific because chemical bonds can only be formed between specific combinations of adsorbate and adsorbent. Because a chemical bond is formed between the adsorbate and the adsorbent, chemical adsorption requires a high adsorption energy to occur. The formation of the adsorbate-adsorbent chemical bond renders dissociation of the adsorbate difficult (Hu and Xu, 2020). Table 1 below presents a comparison of physical and chemical adsorption.

Table 1. Comparison of physical and chemical adsorption (Gupta et al., 2021; Hu and Xu, 2020).

Physical Adsorption	Chemical Adsorption
Caused by Van der Waals forces	Caused by chemical bond formation (ionic or covalent)
Low adsorption energy	High adsorption energy
Dissociation easy	Dissociation difficult

Competitive Adsorption

Competitive adsorption occurs when there are several viable adsorbates for a certain adsorbent. In competitive adsorption, the strength of adsorbate-adsorbent interaction dictates the likelihood of adsorption. Specifically, adsorbates with greater affinity for the adsorbent have a higher probability of being adsorbed than those with weaker affinity, and adsorbates with weaker affinity remain in solution. Furthermore, adsorbates with greater affinity have the capability to displace previously adsorbed substances that have weaker affinity (Tefera et al., 2014). Competitive adsorption is particularly pertinent in natural systems, such as water supplies, which contain a plurality of possible adsorbates. Some studies involving competitive adsorption include the work of Xiao and Thomas (2004) and Tefera et al. (2014).

Adsorption Isotherms

Adsorption can be quantitatively described at equilibrium. Equilibrium is defined as the point at which no more particles will be adsorbed onto the adsorbent surface. The time it takes to reach equilibrium is known as the equilibration time, which can be determined experimentally, as shown by Larous and Meniai (2012).

Adsorption equilibrium can be modeled using equations known as isotherms due to their dependence on temperature (Artioli, 2008). Beyond their dependence on temperature, these equations are based on unique assumptions that describe the properties of the adsorbent surface and the adsorbate-adsorbent interactions (Benzaoui et al., 2017). Some of the most well-known adsorption isotherms are the Freundlich and Langmuir equations.

Freundlich Adsorption Isotherm

The Freundlich adsorption isotherm is used to model adsorption occurring on a heterogeneous surface (Benzaoui et al., 2017). The Freundlich equation (1) can be written as follows:

$$q_e = K_F C_e^{1/n} \quad (1)$$

Alternatively, it can be written in a linearized form (2):

$$\ln K_F + \frac{1}{n} \ln C_e = \ln q_e \quad (2)$$

In eq. (1) and (2), q_e represents the equilibrium adsorption capacity (mg/g), which is the mass of adsorbed substance per mass of adsorbent, and C_e represents the equilibrium concentration of adsorbate remaining in solution (mg/L). Both C_e and q_e can be obtained experimentally. The Freundlich isotherm constant K_F is related to the equilibrium adsorption capacity (L/g). Higher values of K_F indicate stronger adsorption. The unitless constant n is related to the favorability of adsorption; if $1 < n < 10$, adsorption is considered favorable (Benzaoui et al., 2017). Both Freundlich isotherm constants can be obtained from a plot of $\ln q_e$ vs. $\ln C_e$ (Benzaoui et al., 2017; Larous and Meniai, 2012).

Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm is based on 3 assumptions. The first assumption is that the adsorbate forms a complete monolayer on the adsorbent surface, meaning that all adsorbate particles are in contact with the adsorbent (there also exists multilayer adsorption, in which the adsorbate particles form several layers, only one of which is in direct contact with the adsorbent). The second assumption is that each adsorption site can accommodate only a single adsorbate particle. The third assumption is that the adsorbate particles do not interact with one another (Benzaoui et al., 2017). The Langmuir equation (3) can be written as:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \quad (3)$$

Alternatively, it can be written in the following linearized form (4):

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \quad (4)$$

As in the Freundlich equation, q_e represents the equilibrium adsorption capacity (mg/g), and C_e represents the equilibrium concentration of adsorbate in solution (mg/L). The constant K_L represents the Langmuir constant (L/mg) and is related to the free adsorption energy (Larous and Meniai, 2012). Higher values of K_L indicate stronger adsorption. Finally, q_m represents the monolayer adsorption capacity (mg/g), which is the adsorption capacity assuming a complete monolayer is formed (i.e., all adsorption sites are occupied). Both K_L and q_m can be obtained using a plot of $\frac{C_e}{q_e}$ vs. C_e (Benzaoui et al., 2017; Larous and Meniai, 2012).

Additionally, the separation factor R_L , which is a dimensionless quantity used to assess the favorability of adsorption, can be calculated using the Langmuir adsorption isotherm. The equation for R_L (5) is as follows:

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

In eq. (5), C_0 represents the initial concentration of adsorbate in solution (mg/L). If $R_L > 1$, adsorption is considered unfavorable. If $R_L = 1$, adsorption is linear and does not occur (Benzaoui et al., 2017). If $0 < R_L < 1$, adsorption is favorable (Dabhade et al., 2009).

Adsorbents

The investigation of a variety of substances, including cellulosic biomass, lignin, activated carbon, chitosan and seafood wastes, xanthates, zeolites, clay, synthetic polymers, etc., as potential adsorbents for heavy metal contaminants has been ongoing for several decades (Bailey et al., 1999). Several properties are considered when choosing a potential adsorbent: cost efficiency, surface area, pore size distribution, availability of functional area, and polarity (Gupta et al., 2021). Adsorbents derived from biological waste, such as biochar, are particularly attractive due to their lower cost and lesser/no environmental concerns in comparison to other adsorbents (Bilal et al., 2021).

Biochar

Biochar is a solid, carbonaceous product that forms when biomass undergoes thermal decomposition, such as in pyrolysis or hydrothermal carbonization (HTC). Biochar produced via pyrolysis is known as pyrochar, and biochar produced via HTC is known as hydrochar. The primary adsorption mechanisms of heavy metals onto biochar include metal complexation, precipitation, electrostatic attraction, metal- π interaction, ion exchange, and redox reaction (Liu et al., 2021).

Pyrochar is formed when dry biomass undergoes slow pyrolysis at a temperature between 400 – 600°C. Comparatively, hydrochar is formed when wet biomass undergoes HTC at temperatures ranging between 150 – 300 °C (González-Arias et al., 2021). Due to the higher process temperatures of slow pyrolysis, pyrochar normally has a greater carbon content and a larger surface area than hydrochar. The high surface area and porosity of pyrochar contribute to its adsorption of heavy metals (Liu et al., 2021). However, pyrochar has a lower oxygen content than hydrochar and experiences a lower degree of oxygenated functional group (OFG) formation. The reduced quantity of OFGs in pyrochar occurs due to the requirement that pyrolysis feedstock must be dry, whereas the hydrolysis of biomass in the presence of water facilitates the formation of OFGs (Chen et al., 2021). Further restrictive to the formation of OFGs in pyrochar is that temperatures above 400 °C inhibit OFG formation (Delahaye et al., 2020). Therefore, although hydrochar does not have as much surface area or porosity as pyrochar, its OFGs provide sites for heavy metal binding and aid in its ability to adsorb heavy metals (Liu et al., 2021).

Both pyrochar and hydrochar have gained attention in the last decade due to their potency as heavy metal adsorbents. The performance of pyrochar and hydrochar can be compared to activated carbon, which is a carbonaceous product of pyrolysis that undergoes an activation step (such as KOH activation) to improve its adsorptive ability (Mariana et al., 2021). Table 2 below presents the adsorption capacities of lead and copper to pyrochar, hydrochar, and activated carbon. There is significant variation in reported adsorption capacities for the 3 adsorbents, but the performance of biochar is comparable to that of activated carbon. A study by Inyang et al. (2012) found similar results for the adsorption of lead; the adsorption capacity of lead to pyrochar is 40 mg/g, whereas the adsorption capacity of lead to commercially available activated carbon is 20 – 80 mg/g.

Table 2. Heavy metal adsorption capacities of biochar compared to activated carbon (Liu et al., 2021; Mariana et al., 2021).

Adsorbent	Lead Adsorption Capacity (mg/g)	Copper Adsorption Capacity (mg/g)	Reference
Pyrochar	77.3 – 230	17.01 – 486.9	Liu et al., 2021
Hydrochar	92.80 – 241	15.08 – 48.22	Liu et al., 2021
Activated Carbon	53.1 – 253.2	8.9 – 75.99	Mariana et al., 2021

Density Functional Theory

Density functional theory (DFT), which is a computational quantum mechanical tool that calculates the electronic structure of atoms and molecules, can be used to quantitatively model the adsorption of heavy metals to adsorbents (Baseden, 2014). Several recent studies on the adsorption of heavy metals to biochar that incorporate DFT calculations alongside experimental results include those of Feng et al. (2022), Chen et al. (2021), Cheng et al. (2021), Zhao et al. (2021), Chen et al. (2020), Delahaye et al. (2020), and Zhu et al. (2020). Specifically, these studies use DFT to assess adsorbate-adsorbent geometries, as well as adsorption energies.

The Schrödinger Equation and Electron Density

DFT strives to answer the question of how the energy of a molecule changes based on the position of its nuclei and electrons. The positions of the nuclei in a molecule are particularly important because they define the motion, and therefore the energy, of the electrons. The lowest energy state is defined as the ground state, which can be calculated by using the Schrödinger equation (6), shown below (Sholl & Steckel, 2009):

$$H\psi = E\psi \quad (6)$$

In eq. (6), H represents the Hamiltonian operator, which corresponds to the total energy of the system, ψ represents the Hamiltonian's eigenstates, and E represents the eigenvalues of ψ . For the energy of a molecule, ψ represents the electronic wave function, which is a function of the spatial coordinates of each electron in the modeled system, and E represents the ground-state energy of the electrons. (Sholl & Steckel, 2009).

The Schrödinger equation is a many-body problem. This is because the Hamiltonian operator, H , is itself dependent on the spatial coordinates of the electrons, meaning that the electronic wave function, ψ , must be solved simultaneously with the Hamiltonian operator. Furthermore, because each electron is associated with 3 dimensions, the wave function can require thousands of dimensions to solve when larger molecules are considered, which can complicate the solution of the Schrödinger equation (Sholl & Steckel, 2009). To bypass this complexity, DFT calculations make use of electron density; this property is particularly pertinent because the total electronic energy of an atomic system is a functional of the electron density, as proven by Hohenberg and Kohn (Baseden, 2014). The equation for electron density can be written as follows (Sholl & Steckel, 2009):

$$n(\mathbf{r}) = 2 \sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) \quad (7)$$

In eq. (7), $n(\mathbf{r})$ represents the density of electrons at a specified position, $\mathbf{r}$ represents the 3 dimensions of position, and the summation represents the probability that an electron in its individual wave function $\psi_i(\mathbf{r})$ is located at the previously specified position. The factor of 2 appears as an effect of the Pauli exclusion principle. The electron density has only 3 dimensions in comparison with the original electronic wave function of the Schrödinger equation which has 3 dimensions for every electron in the system (Sholl & Steckel, 2009). An additional advantage of

electron density is that, unlike Schrödinger's wave function, it is experimentally observable (Baseden, 2014).

Total Energy as a Functional of Electron Density

As mentioned previously, the total energy of an atomic system is a functional of electron density. Furthermore, the electron density that yields the minimum energy, or the ground-state energy, is considered the true electron density and yields a solution analogous to that of the Schrödinger equation. Therefore, the ground-state energy of a molecule can be calculated if the electron density is known. The electron density itself can be determined by solving the Kohn-Sham equations, which is a set of single-electron wave functions that depend on $\mathbf{r}$ (Sholl & Steckel, 2009).

Solving a DFT Calculation

There is a cyclical nature to the solving of a DFT calculation. This phenomenon arises because the solution of the Kohn-Sham equations requires that the electron density is known. To solve a DFT calculation, an initial electron density must first be chosen. Then, the Kohn-Sham equations must be solved using the initial electron density. The electron density can then be determined by using the calculated Kohn-Sham equations, and the determined electron density can be compared to the initial electron density. If the two electron densities are equal (to a certain precision), then the calculated electron density is the ground-state electron density and can be used to determine the total energy of the molecule. However, if the densities differ, the initial electron density must be re-chosen. This process continues until the ground-state electron density is identified (Sholl & Steckel, 2009).

Exchange-Correlation Energy Functionals

Exchange-correlation energy provides a critical contribution to the molecular energy arising from electron-electron interactions, but it is a functional with an unknown form. An issue with the Kohn-Sham equations arises from the exchange-correlation energy, which is required for the calculation of the Kohn-Sham equations (Sholl & Steckel, 2009). Furthermore, determining the exchange-correlation energy exactly can be more computationally expensive than explicitly solving the Schrödinger equation. To address this issue, approximations of the exchange-correlation energy, such as the local density approximation (LDA) functional and the generalized gradient approximation (GGA) functional were developed for DFT calculations. Hybrid functionals, which incorporate some aspect of Hartree-Fock exchange, have also been developed (Burke, 2012). The Becke, 3-parameter, Lee–Yang–Parr (B3LYP) functional is an example of a hybrid functional. The selection of an exchange-correlation energy functional is not always straightforward, as it can influence not only the accuracy of the DFT calculation but also the computational cost of the calculation (Sholl & Steckel, 2009).

Basis Sets

DFT calculations, which traditionally compute the electron density rather than the electron wave function, can also incorporate wave-function-based methods to compute some

part of the electronic energy (Baseden, 2014). Wave-function-based methods are advantageous over DFT calculations because they can converge to the Schrödinger equation's exact solution, given infinite time (Sholl & Steckel, 2009). The incorporation of wave-function-based methods necessitates the selection of a basis set, which is a set of functions that approximates the spin orbitals of the system. Generally, a DFT calculation using a basis set with more functions will produce a solution that is in closer agreement with the Schrödinger equation. However, using such a basis set is associated with an increased computational cost (Sholl & Steckel, 2009). Basis sets are also developed to be applied to specific elements – the 6-21G basis set, for example, applies only to H – Cl (inclusive) on the periodic table (Gaussian, 2021).

Limitations

DFT has seen widespread application due to its fair accuracy in predicting electronic structures of molecules and low computational cost (Baseden, 2014). However, the method has several limitations. Because DFT is approximative, it may not produce sufficiently accurate results (for example, the acceptable error for reaction energies is typically between 0.5 – 1 kcal/mol). DFT calculations also have difficulty modeling Van der Waals interactions, which are not accurately captured by basis sets (Schwabe & Grimme, 2008). This is particularly harmful in modeling of larger molecules, where dispersion forces have a much greater impact on the electronic structure than exchange repulsion (Grimme et al., 2007). The modeling of anions may also be inaccurate in DFT calculations because the electrons are essentially unbound (Burke, 2012).

Methodology

Computational Methods

All DFT simulations were performed on WebMO (Schmidt and Polik, 2020) using Gaussian 09 (Frisch et al., 2009). The Becke, 3-parameter, Lee-Yang-Parr (B3LYP) exchange-correlation functional and the LANL2DZ basis set were used. To account for water solvation, the polarizable continuum model (PCM) was used with water as the chosen solvent. The UHF keyword was used for all simulations to enforce use of the unrestricted Hartree-Fock Hamiltonian.

Geometry optimization calculations were run on subunits of a proposed molecular structure of glucose hydrochar in unpublished work by Schmidt-Rohr. The structure was determined using NMR spectral results (Johnson and Schmidt-Rohr, 2014). Using this structure, 10 potential binding sites were chosen throughout the molecule, shown in green circles in Figure 1. The bonds at the outer limits of the drawn boundaries of each binding site were cut and joined to a hydrogen instead. Additionally, simulations were run where the bonds were joined to methyl, phenyl, and furan groups instead of a hydrogen. In the DFT simulations, the acidic hydrogens (present in hydroxyl and carboxyl groups) in the sites were replaced with a potassium (K⁺) to represent the effects of KOH-activation. As several sites (1, 3, 4, and 8) had several acidic hydrogens, only one acidic hydrogen was replaced at a time, and the position of the acidic hydrogen was denoted with a letter (i.e., 4A, 4B, and 4C). Sites without acidic hydrogens were simulated as given. These geometries are presented in Appendix A.

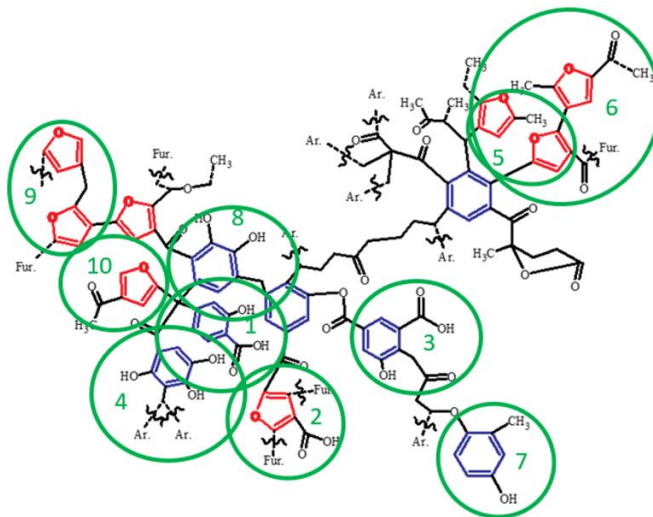


Figure 1. Proposed molecular structure of glucose hydrochar with binding sites circled (Schmidt-Rohr, unpublished).

Potassium Exchange Energy

The potassium exchange energy was determined after obtaining the optimized geometries of each binding site. First, the potassium ion was replaced with a heavy metal cation, such as copper (II) or lead (II). Then, individual heavy metal cations and potassium cations were

simulated using the geometry optimization calculation. Then, the UB3LYP energy was obtained for each of the four species, namely the solvated metal cation (MC) and the default binding site (BS), which were the reactants, and the solvated potassium cation (K+) and the binding site complexed with the metal cation (MBS), which were the products. The potassium exchange energy in kJ/mol was calculated using eq. (8) below.

$$\begin{aligned} \text{Potassium exchange energy} &= E_{\text{products}} - E_{\text{reactants}} \\ &= [(E_{\text{MBS}} + E_{\text{K}^+}) - (E_{\text{BS}} + E_{\text{MC}})] \end{aligned} \quad (8)$$

For binding sites without any acidic hydrogens (5, 6, 9, and 10), a modified procedure was followed. Instead of replacing a potassium ion, the heavy metal cation was placed in various positions around the binding site, and the lowest energy configuration was chosen. the enthalpy was then calculated using eq. (9) below:

$$\begin{aligned} \text{Potassium - exchange energy} &= E_{\text{products}} - E_{\text{reactants}} \\ &= [(E_{\text{MBS}}) - (E_{\text{BS}} + E_{\text{MC}})] \end{aligned} \quad (9)$$

Although the enthalpy determined by eq. (9) did not account for ion exchange, it was assessed alongside with the potassium exchange energies. The term potassium exchange energy was used in favor of adsorption energy to prevent confusion due to the potassium exchange energies having uncharacteristically high values in comparison to experimentally determined adsorption energies. Experimental adsorption energies typically vary from 0 to -80 kJ/mol (Inglezakis and Zorpas, 2012).

Explicit Water Solvation Modeling

To better account for the effects of water solvation on the adsorption of Cu(II) and Pb(II) to hydrothermal char, explicit water molecules were added to the geometries of binding sites with acidic hydrogens (1A, 1B, 2, 3A, 3B, 4A, 4B, 4C, 7, 8A, and 8B). All explicit water solvation calculations included PCM to account for water solvation, as was the case for all other DFT calculations. Explicit water solvation was modeled first by adding one water molecule to interact with the metal cation while it was complexed with the binding site. Specifically, for the reactant binding site, a water molecule was complexed with the potassium cation, and for the product binding site, a water molecule was complexed with either the Cu(II) or Pb(II) cation. Water molecules were not added to the solvated metal cation (MC) or the solvated potassium (K+). These calculations were then redone with the inclusion of two water molecules.

Linear Fitting of Physical Properties

The potassium exchange energy was determined for copper (II) and lead (II) for every binding site. Then, selecting three of the lowest potassium exchange energy binding sites (4A, 4B, and 4C) and another binding site (3B), the potassium exchange energy was determined for alkali metals, alkaline earth metals, transition metals (including both noble metals and non-noble metals), post-transition metals, and metalloids. These metals were separated into the following four groupings: alkali and alkaline earth metals, non-noble transition metals, noble transition

metals, and post-transition metals and metalloids. Table 3 lists the assessed metals and their corresponding groupings.

Table 3. Assessed heavy metals and groupings. Effective ionic radii are from Shannon (1976). Silver is listed as a noble metal according to Brooks (1992), and copper is listed as a noble metal according to Whitten (2014).

Metal	Charge	Effective Ionic Radius (Å)	Grouping
Sodium	+1	1.02	Alkali and alkali earth metals
Beryllium	+2	0.45	Alkali and alkali earth metals
Magnesium	+2	0.72	Alkali and alkali earth metals
Calcium	+2	1.00	Alkali and alkali earth metals
Barium	+2	1.35	Alkali and alkali earth metals
Titanium	+4	0.605	Non-noble transition metals
Iron	+2	0.61	Non-noble transition metals
Chromium	+3	0.615	Non-noble transition metals
Vanadium	+3	0.64	Non-noble transition metals
Molybdenum	+3	0.69	Non-noble transition metals
Nickel	+2	0.69	Non-noble transition metals
Zinc	+2	0.74	Non-noble transition metals
Cadmium	+2	0.95	Non-noble transition metals
Mercury	+2	1.02	Non-noble transition metals
Copper	+2	0.73	Noble transition metals
Platinum	+2	0.80	Noble transition metals
Gold	+3	0.85	Noble transition metals
Palladium	+2	0.86	Noble transition metals
Silver	+1	1.15	Noble transition metals
Aluminum	+3	0.535	Post-transition metals and metalloids
Gallium	+3	0.62	Post-transition metals and metalloids
Thallium	+3	0.885	Post-transition metals and metalloids
Arsenic	+3	0.58	Post-transition metals and metalloids
Bismuth	+3	1.03	Post-transition metals and metalloids
Lead	+2	1.19	Post-transition metals and metalloids
Antimony	+3	0.76	Post-transition metals and metalloids

Then, the formal surface charge density (eq. (10)), Born energy (eq. (11)), and electric potential energy (eq. (12)) were calculated for each metal (Israelachvili, 2012). For each of the four groups, linear fitting between the potassium exchange energy and the three properties was performed using OriginLab.

Formal Surface Charge Density

The formal surface charge density was determined using the following equation:

$$FSCD = \frac{1.602 \times 10^{-19} Q_{cation}}{4\pi r_E^2} \quad (10)$$

In eq. (10), Q_{cation} represents the formal charge of the metal cation in Coulombs. In the denominator, r_E is the effective ionic radius of the cation in meters. $FSCD$ represents the formal surface charge density, which is the charge per surface area of the cation in Coulombs/m². This property accounts for the cation's charge and size, but neglects environmental effects.

Born Energy

The Born energy was calculated using the following equation:

$$BE = \frac{Q_{cation}^2}{8\pi\epsilon_0\epsilon r_E} \quad (11)$$

In eq. (11), ϵ_0 represents vacuum permittivity in Farads per meter. ϵ represents the dielectric permittivity of the medium, which in this case is water at 20 degrees Celsius (Archer and Wang, 1990). BE represents the Born energy (also known as solvation energy) of the cation in kJ/mol. The Born energy represents the energy required to form the cation in its specific configuration in the medium designated by ϵ . Alternatively, it can be understood as the energy required to maintain its charge against its own electrostatic repulsion (Israelachvili, 2012). This property accounts for the medium in which the cation is present in addition to the cation's charge and size.

Electric Potential Energy

The electric potential energy was determined using the following equation:

$$EPE = \frac{Q_{cation}Q_{anion}}{4\pi\epsilon_0\epsilon r} \quad (12)$$

In eq. (12), Q_{anion} represents the formal charge of the oxygen anion in Coulombs. The rightmost term in the denominator, r , is the sum of the radii of the heavy metal cation and the oxygen anion in meters. EPE represents the electric potential energy in kJ/mol. The electric potential energy is a measurement of free energy between two charged particles, or, in this case, the metal cation and an oxygen anion. The quantity is negative between a cation and an anion due to their opposing and attractive charges (Israelachvili, 2012). This property accounts for the cation's charge and size, the medium, and the anion's charge and size.

Experimental Methods

Materials

Table 4 below lists the chemical reagents used for experimentation. Deionized (DI) water used for hydrochar washing and preparation of solutions was purified to a resistivity of at least 17.9 M Ω .

Table 4. Chemical reagents used for experimentation.

Chemical	Purity	Origin
D-(+)-glucose	$\geq 99.5\%$	Sigma-Aldrich
Potassium hydroxide	$\geq 85\%$	Sigma-Aldrich
Copper (II) nitrate hemi(pentahydrate)	$\geq 98\%$	Sigma-Aldrich
Lead (II) nitrate	$\geq 99\%$	Sigma-Aldrich

Hydrochar Synthesis

The synthesis of hydrochar was adapted from Delahaye et al. (2020). First, 28.04 g of D-(+)-glucose was measured on a weighing boat. A 500 mL beaker was filled with 50 mL DI water, and then the D-(+)-glucose was transferred from the weighing boat into the beaker. DI water was added to the beaker up to the 100 mL mark, and the D-(+)-glucose was dissolved via mixing with a spatula. The solution was then loaded into a 160 cm³ PTFE-lined reactor, which was then placed into a stainless-steel autoclave. The autoclave was secured shut with bolts. The autoclave was placed in an oven at room temperature, which was heated to 180 °C at a rate of approximately 10 °C/minute. The autoclave remained in the oven at 180 °C for 8 hours prior to removal. The autoclave was left at room temperature for 24 hours. The autoclave was unbolted, and the reactor was taken out.

Afterwards, the hydrochar was filtered for removal of soluble organic materials based on the procedures described by Delahaye et al. (2020). The carbonaceous product was first transferred from the reactor into a 500 mL beaker. Next, 300 mL ethanol and 300 mL DI water were poured into two individual 500 mL beakers. A 1000 mL filtering flask was connected to a vacuum. A funnel was connected at the mouth of the flask, and a piece of filter paper was positioned on it. The carbonaceous product was poured from its 500 mL beaker onto the filter paper, and the vacuum was turned on. Then, approximately 100 mL DI water was poured over the carbonaceous product. After the DI water passed through the filter, 100 mL ethanol was poured over the product. This step was repeated twice, such that the carbonaceous product was washed with 300 mL DI water and 300 mL ethanol in total. The vacuum filtration setup is shown in Figure 2 below.



Figure 2. Vacuum filtration setup. The vacuum was connected to the 1000 mL filtering flask with tubing. A funnel was connected to the mouth of the flask, and filter paper (not visible) was placed in the funnel. The brown-colored liquid in the flask is the filtered DI water, ethanol, and soluble organic materials.

The saturated hydrochar was then transferred from the filter paper into three crucibles. The crucibles were placed in an oven that was preheated to 65 °C. They remained in the oven for 24 hours to allow for drying to occur. After the 24-hour period had concluded, the crucibles were removed from the oven, and the mass of the hydrochar was measured to be 6.92 g. The dried hydrochar was then stored in airtight vials (Delahaye et al., 2020).

Hydrochar Activation

The KOH-activation of hydrochar was adapted from Delahaye et al. (2020). First, 56.12 g KOH was measured on a weighing boat. A 1000 mL beaker was filled with 400 mL DI water, and the solid KOH was transferred into the beaker. After the KOH was dissolved, the beaker was filled with DI water to the 500 mL mark, yielding a 2 N KOH solution. Then, 2.22 g hydrochar was measured on a weighing boat. The hydrochar was placed into the 500 mL 2 N KOH solution, where it was left for 4 hours at room temperature. Soluble contaminants were then filtered from the solution using the same filtering procedures and setup (Figure 2) described in the previous section, washing the KOH-activated hydrochar with 100 mL DI water and 100 mL ethanol three times.

The saturated KOH-activated hydrochar was then transferred from the filter paper into a crucible, which was placed in an oven at room temperature. The oven was then heated to 100 °C at a rate of approximately 10 °C/minute, and the sample was left to dry in the oven for 24 hours. After the 24-hour period had concluded, the crucible was removed from the oven. The hydrochar was then ground using a mortar and pestle prior to being stored in airtight vials (Delahaye et al., 2020).

Heavy Metal Solution Preparation

Two 0.05 M solutions of copper (II) nitrate and lead (II) nitrate were prepared to be used in the competitive adsorption experiment. First, two 1000 mL beakers were each filled with 400 mL DI water. To prepare the copper nitrate solution, 5.9949 g copper (II) nitrate hemi(pentahydrate) was measured on a weighing boat prior to being added to one of the 1000 mL beakers containing 400 mL DI water. The copper (II) nitrate hemi(pentahydrate) was dissolved in the DI water by mixing with a spatula. Then, DI water was added up to the 500 mL mark, yielding a solution of ~0.05 M copper (II). The copper nitrate solution was poured into three 200 mL glass bottles that were shut with a screw cap. To prepare the lead nitrate solution, 8.3929 g lead (II) nitrate was measured on a weighing boat prior to being added to the remaining 1000 mL beaker containing 400 mL DI water. The lead (II) nitrate was dissolved in the DI water by mixing with a spatula. Then, DI water was added up to the 500 mL mark, yielding a solution of ~0.05 M lead (II). The lead nitrate solution was then poured into three 200 mL glass bottles that were shut with a screw cap.

Competitive Adsorption Experiment

A binary competitive adsorption experiment was performed to assess the adsorption of copper (II) versus lead (II) by the KOH-activated hydrochar. The concentrations of the two metal ions were varied in three ratios: 1:2 (molar concentration copper (II) to molar concentration lead (II)), 1:1, and 2:1 (Xiao and Thomas, 2004). Using a transfer pipette, a vial was filled with 10 mL of the 0.05 M copper (II) solution and 20 mL of the 0.05 M lead (II) solution. Similarly, a second vial was filled with 15 mL of the 0.05 M copper (II) solution and 15 mL of the 0.05 M lead (II) solution. A third vial was filled with 20 mL of the 0.05 M copper (II) solution and 10 mL of the 0.05 M lead (II) solution. These three vials represented 1:2, 1:1, and 2:1 molar concentrations of copper (II) to lead (II). Then, three samples of KOH-activated hydrochar weighing 0.1 g each were measured using individual weighing boats (Xiao and Thomas, 2004). One KOH-activated hydrochar sample was placed into each of the three vials, and the solution was allowed to equilibrate for 48 hours. Equilibration time had been previously determined to be 24 hours by experiment, but this time was doubled for safety. At the end of the 48-hour period, the samples were filtered using the setup shown in Figure 2, and the liquid was recovered and transferred to a vial. No washing was performed in this filtering step. The volume of the recovered liquid was measured. The copper (II) and lead (II) content of the samples was determined using inductively coupled plasma mass spectroscopy (ICP-MS). Three vials of 1:2, 1:1, and 2:1 (molar concentration copper (II) to molar concentration lead (II)) were then prepared identically as previously described, but KOH-activated hydrochar was omitted. The experiment was performed in duplicate. Next, ICP-MS was used to determine the copper (II) and lead (II) concentrations of the samples. Finally, the average adsorption capacity for the three cases was determined using the following equation:

$$\text{Adsorption capacity} \left(\frac{\text{mmol}}{\text{g}} \right) = \frac{\text{mass}_{\text{metal,initial}} - \text{mass}_{\text{metal,final}} (\text{mmol})}{\text{mass}_{\text{KOH-activated hydrochar}} (\text{g})} \quad (13)$$

The adsorption capacities calculated from eq. (13) were then compared to determine if copper (II) or lead (II) had a greater affinity for the produced KOH-activated hydrochar.

Results and Discussion

Distribution of Oxygen-Containing Functional Groups

The oxygen-containing functional groups that interact with heavy metal cations are presented below in Table 5. The predicted oxygen-containing functional groups in the simulated hydrochar molecule are hydroxyl groups, carboxyl groups, carbonyl groups, and furans. Hydroxyl groups are the most common interactive chemical group, with 7 of the 15 binding sites containing at least one hydroxyl group. Carboxyl, furan, and carbonyl groups appear at the same frequency, each being present on 3 of the 15 binding sites. 11 of the 15 binding sites have acidic hydrogens, which are present in hydroxyl and carboxyl groups.

Table 5. Functional groups present on each binding site. Binding sites labelled with a * do not contain an acidic hydrogen.

Binding Site	Interactive Functional Group 1	Interactive Functional Group 2	Interactive Functional Group 3
1A	Hydroxyl	Carboxyl	-
1B	Carboxyl	-	-
2	Carboxyl	-	-
3A	Carboxyl	-	-
3B	Carbonyl	Hydroxyl	-
4A	Hydroxyl	Hydroxyl	-
4B	Hydroxyl	Hydroxyl	-
4C	Hydroxyl	-	-
5*	Furan	Furan	-
6*	Carbonyl	Furan	Furan
7	Hydroxyl	-	-
8A	Hydroxyl	Hydroxyl	-
8B	Hydroxyl	-	-
9*	Furan	Furan	-
10*	Carbonyl		-

DFT Simulation of Copper (II) and Lead (II) Adsorption to Hydrothermal Char

DFT geometry optimization calculations were performed on WebMO using Gaussian 09 to model the binding sites shown in Figure 1. The B3LYP exchange-correlation functional and the LANL2DZ basis set were used, including the PCM with water as the chosen solvent. Acidic hydrogens were replaced with potassium ions in the optimized geometries, and the energy to replace the acidic hydrogens with either copper (II) or lead (II) was calculated. For sites without acidic hydrogens, copper (II) or lead (II) were placed such that the molecule reached its lowest energy configuration, and the energy was calculated.

Potassium Exchange Energies

The energies are presented in Figure 3a, arranged from least negative on the left and right sides to most negative in the center. The potassium exchange energies of lead range from -132 kJ/mol to -379 kJ/mol, with a mean value of -289 kJ/mol. The potassium exchange energies of copper range from -361 kJ/mol to -653 kJ/mol, with a mean value of -551 kJ/mol. Because the potassium exchange energies of both copper and lead are negative, the replacement of potassium with these heavy metal cations is a favorable process that leads to a more thermodynamically stable configuration of the binding site. Additionally, for all binding sites, the potassium exchange energy of copper is more negative than that of lead. The greater negativity of the copper potassium exchange energies indicates that it is more energetically favorable to replace a potassium ion (K⁺) with a copper ion (Cu²⁺) than with a lead ion (Pb²⁺).

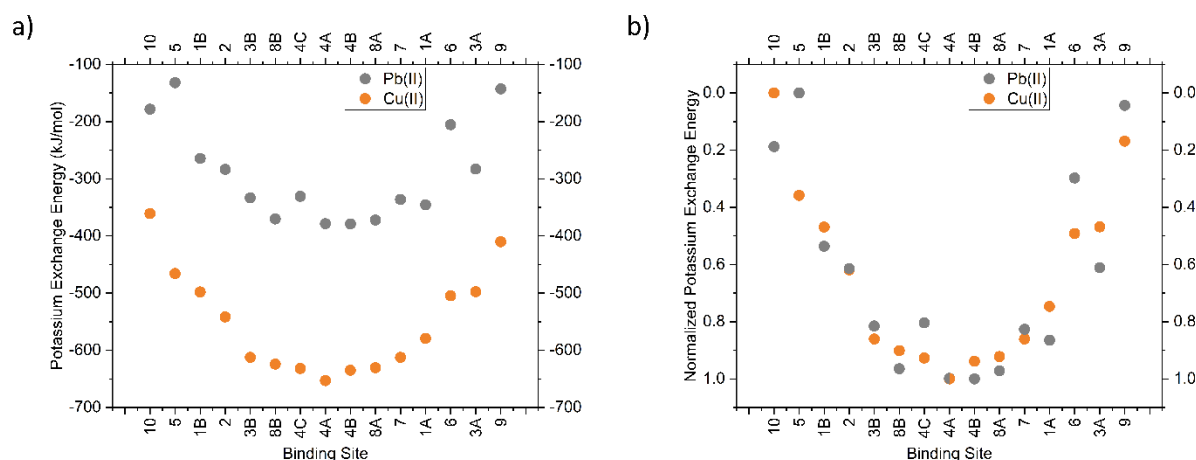


Figure 3. a) Potassium exchange energies for Cu(II) and Pb(II) for the case where cut bonds were joined to hydrogens. b) Normalized potassium exchange energies for Cu(II) and Pb(II) for the case where cut bonds were joined to hydrogens.

However, it is important to note that the calculated potassium exchange energies are much higher than experimentally determined adsorption energies, which are normally less negative than -80 kJ/mol (Inglezakis and Zorpas, 2012). Therefore, the model should be refined in future work. A normalization was performed to analyze the data without considering any errors that caused the uncharacteristically negative energies. These normalized potassium exchange energies are presented in Figure 3b. The normalized values were calculated with the following equation:

$$Normalized\ KEE_i = \frac{KEE_i - KEE_{max}}{KEE_{min} - KEE_{max}} \quad (14)$$

In eq. (14), KEE is an abbreviation for potassium exchange energy. The subscript “ i ” denotes the potassium exchange energy at a specified binding site, and “ max ” and “ min ” correspond to the most and least negative exchange energies respectively.

As seen in Figure 3b, the potassium exchange energy curves for copper and lead follow a similar “U”-shaped pattern. Generally, the sites containing at least one hydroxyl group (1A, 4A, 4B, 4C, 7 8A, and 8B) have more negative potassium exchange energies than sites that do not (1B, 3A, 5, 6, 9, and 10). More specifically, binding sites 4A and 4B have the most negative potassium exchange energy for both heavy metal cations. In binding sites 4A and 4B, the heavy metal cation is bound by two hydroxyl groups, which could explain the high favorability of potassium exchange.

Bond Length

Figures 4a and 4b show the configurations of binding site 4B complexed with copper and lead, respectively. As seen in Figure 4, both copper and lead are approximately 2 angstroms away from the oxygen anions, indicating that chemical bonding is occurring between the cation-anion pair. It is also noted that the copper cation has shorter bond lengths than the lead cation. This could be due to lead having a greater atomic radius than copper (0.73 vs. 1.19 Å), but it also indicates that lead is bound less tightly to the binding site than copper.

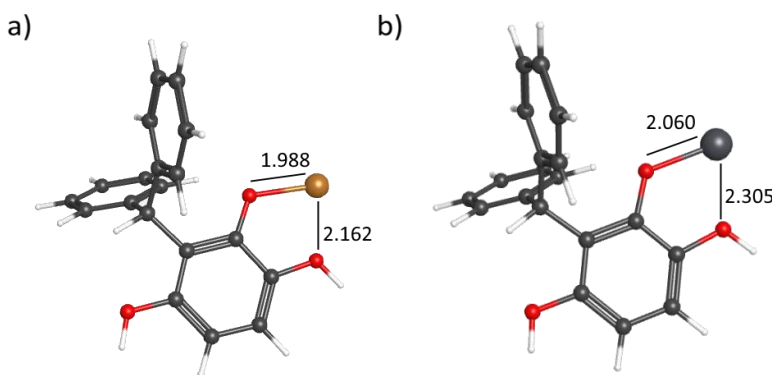


Figure 4. a) Binding site 4B complexed with Cu(II). b) Binding site 4B complexed with Pb(II). Bond length is in angstroms.

Copper has shorter bond lengths with oxygen than lead is for all other acidic-hydrogen-containing binding sites, as seen in Table 6 below. The average bond length between copper (II) and oxygen is 2.116 Å, and the average bond length between lead (II) and oxygen is 2.194 Å. Because bond length is generally inversely proportional to bond dissociation energy, the shorter bond length between copper and oxygen agrees with the potassium exchange energy of copper being more negative than that of lead.

Table 6. Metal cation – oxygen (M-O) bond lengths for binding sites complexed with either Cu(II) or Pb(II). For sites where the heavy metal cation interacts with only one oxygen atom, the bond is named “Short.” For sites where the heavy metal cation interacts with two oxygen atoms, the bonds are named “Short” or “Long” relative to one another.

Binding Site	Cu(II) M-O Bond Length (Å)		Pb(II) M-O Bond Length (Å)	
	Short	Long	Short	Long
1A	1.943	2.095	2.017	2.342

1B	1.933	3.163	2.279	2.290
2	1.916	2.975	2.266	2.271
3A	1.986	1.99	2.272	2.288
3B	1.921	2.013	2.079	2.413
4A	1.999	2.141	2.055	2.315
4B	1.988	2.162	2.060	2.305
4C	1.901	-	1.947	-
7	1.898	-	1.941	-
8A	2.000	2.148	2.057	2.315
8B	1.991	2.155	2.059	2.313
Average (Å)	2.116		2.194	

Explicit Water Solvation Modeling

Each binding site with acidic hydrogens (1A, 1B, 2, 3A, 3B, 4A, 4B, 4C, 7, 8A, and 8B) was modeled to account for water solvation effects in the exchange of a potassium ion with either a copper (II) ion or a lead (II) ion. Initially, one water molecule was added to complex with the metal cation. Then, a second water molecule was added. The potassium exchange energy was then calculated for each binding site. Figure 5 below shows the geometries of binding site 7 with explicit water solvation for potassium (5a – 5c), copper (5d – 5f), and lead (5g – 5i).

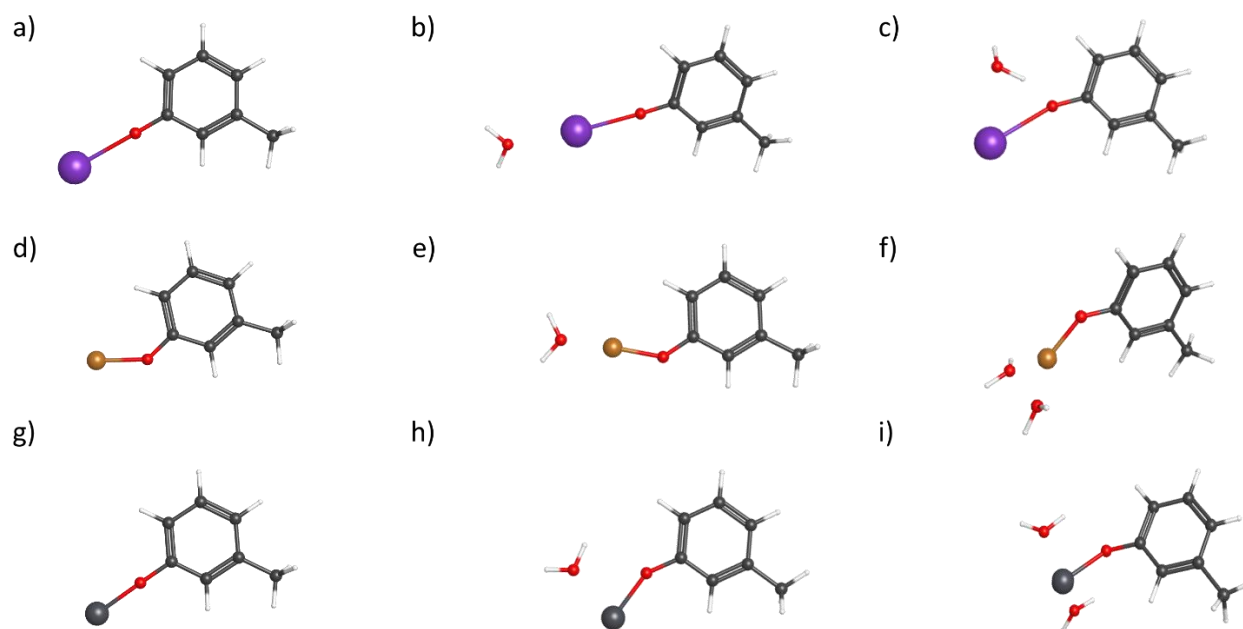


Figure 5. Geometries of binding site 7 with and without explicit solvation. a), b), and c) show binding site 7 with a bound potassium cation and 0, 1, and 2 water molecules, respectively. d), e), and f) show binding site 7 with a bound copper (II) cation and 0, 1, and 2 water molecules, respectively. g), h), and i) show binding site 7 with a bound lead (II) cation and 0, 1, and 2 water molecules, respectively.

Potassium Exchange Energies

The calculated potassium exchange energies for the one water molecule explicit solvation case are presented in Figure 6a, arranged in the same binding site order as in Figure 3. The potassium exchange energies of lead range from -347 kJ/mol to -435 kJ/mol, with a mean value of -392 kJ/mol. The potassium exchange energies of copper range from -604 kJ/mol to -749 kJ/mol, with a mean value of -702 kJ/mol. Figure 7a presents the calculated potassium exchange energies for the two water molecule explicit solvation case. With two water molecules, the potassium exchange energies of lead range from -342 kJ/mol to -451 kJ/mol, with a mean value of -403 kJ/mol. For copper, the potassium exchange energies range from -605 kJ/mol to -750 kJ/mol, with a mean value of -711 kJ/mol.

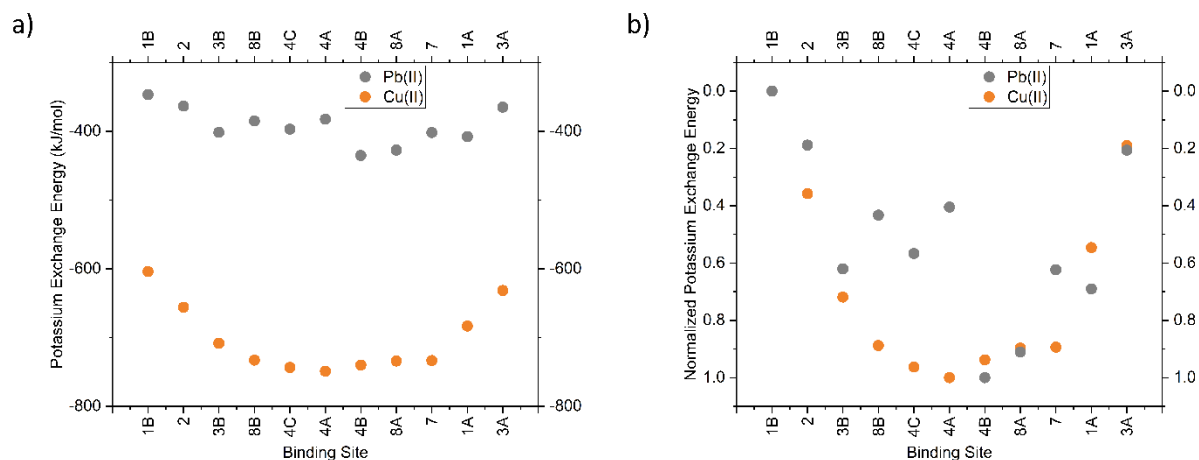


Figure 6. a) Potassium exchange energies for Cu(II) and Pb(II) for the case where one water molecule is added to the geometry. b) Normalized potassium exchange energies for Cu(II) and Pb(II) for the case where one water molecule is added to the geometry.

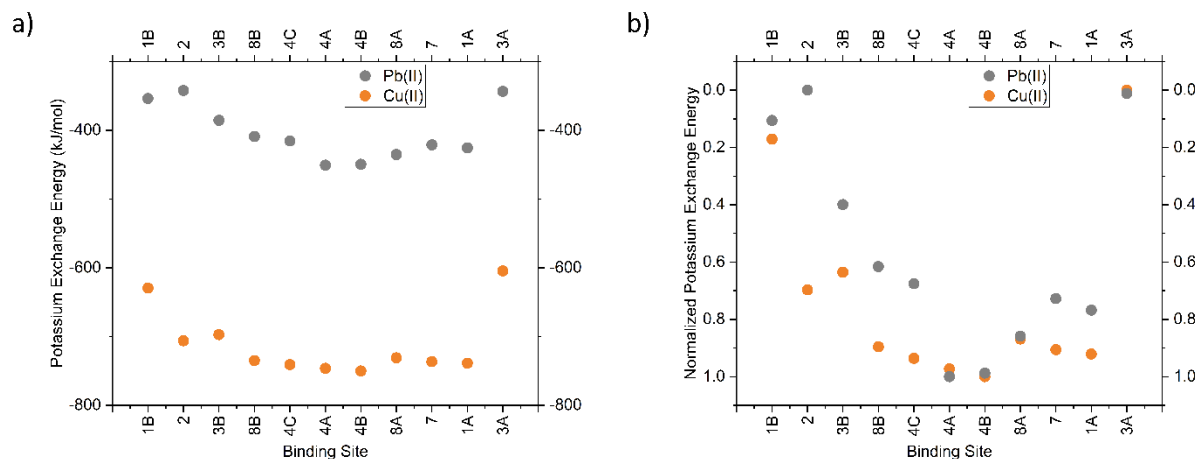


Figure 7. a) Potassium exchange energies for Cu(II) and Pb(II) for the case where two water molecules are added to the geometry. b) Normalized potassium exchange energies for Cu(II) and Pb(II) for the case where two water molecules are added to the geometry.

As can be seen in Figures 6b and 7b, which present the normalized potassium exchange energies using eq. (11), the most negative potassium exchange energies are found in binding site 4. The “U”-shaped pattern seen in Figure 3b appears for copper most strongly in Figure 6b, and it appears to a lesser extent in Figure 7b. This pattern is not clearly visible for lead in Figure 6b due to the energies of sites 8B, 4C, 4A, 4B, 8A, and 7. However, the “U”-shape is somewhat visible for lead in Figure 7b.

Error in Modeling Explicit Water Solvation

Explicit water molecules were incorporated into the modeling with the goal of making the potassium exchange energy have a more positive value to match experimental values for adsorption energy (Inglezakis and Zorpas, 2012). Instead, it was found that adding explicit water molecules made the potassium exchange energy more negative (Table 7). Therefore, it is likely that the effects of solvation in water were not modeled accurately. This could be due to incorrect placement of water molecules in the binding site geometries or an inadequate number of water molecules included in the simulations. The error could have also been due to incorrect inclusion of water molecules in the potassium exchange energy calculations. The water molecules were added to the reactant and product binding site geometries while neglecting solvation effects on the metal cation geometries, which may have been incorrect. Possible methods to improve the explicit water solvation calculations are discussed in Conclusions.

Table 7. Average potassium exchange energies for Cu(II) and Pb(II) when modeled with 0, 1, or 2 explicit water molecules.

Number of Water Molecules	Average Cu(II) Potassium Exchange Energy (kJ/mol)	Average Pb(II) Potassium Exchange Energy (kJ/mol)
0 (Figure 3)	-551	-289
1 (Figure 6)	-702	-392
2 (Figure 7)	-711	-403

Linear Fitting of Physical Properties

Formal surface charge density (eq. (10)), Born energy (eq. (11)), and electric potential energy (eq. (12)) were correlated with potassium exchange energy for various metal ions (Table 3), including alkali metals, alkaline earth metals, noble and non-noble transition metals, post-transition metals, and metalloids. DFT geometry optimization calculations were performed to calculate the potassium exchange energy for these ions on binding sites 4A, 4B, 4C, and 3B. Binding sites 4A, 4B, and 4C were chosen because these sites had the most negative potassium exchange energies for both copper and lead (Figure 3B). Binding site 3B was included because this site yielded the most negative potassium exchange energy when the metal ion interacted with a carbonyl group, which is a functional group that does not contain an acidic hydrogen. For each of the four groupings presented in Table 3, the energies of these 4 sites were plotted against the aforementioned physical properties, and a linear regression with the following equation was performed:

$$y = a + bx \quad (15)$$

In eq. (15), a is the y -intercept and b is the slope of the regression curve. The two variables, x and y , represent the calculated value associated with the physical property and the potassium exchange energy, respectively.

Formal Surface Charge Density

The coefficients of the linear regression equation and the adjusted R^2 values for the potassium exchange energy versus the formal surface charge density are presented in Table 8. As seen in Table 8, potassium exchange energy is strongly correlated with formal surface charge density for the alkali and alkaline earth metals group ($R^2 = 0.98$), as well as for the non-noble transition metals group ($R^2 = 0.96$). Potassium exchange energy is moderately correlated with formal surface charge density for the noble transition metals group ($R^2 = 0.61$) and the post-transition metals and metalloids group ($R^2 = 0.60$). Because the formal surface charge density is based on radius and charge of the cation, these results indicate that the potassium exchange energy of alkali and alkaline earth metals and non-noble transition metals can be strongly predicted based on cation properties. Figures 8a and 8b present the graphs of the potassium exchange energy versus the formal surface charge density for the alkali and alkaline earth metals group and the non-noble transition metals group, which had the highest R^2 values.

Table 8. Linear regression results for potassium exchange energy versus formal surface charge density, where the coefficients a and b are based on eq. (15).

Grouping	Alkali and alkaline earth metals	Non-noble transition metals	Noble transition metals	Post-transition metals and metalloids
a	30	370	300	-600
b	-37	-130	-250	-70
R^2	0.98	0.96	0.61	0.60

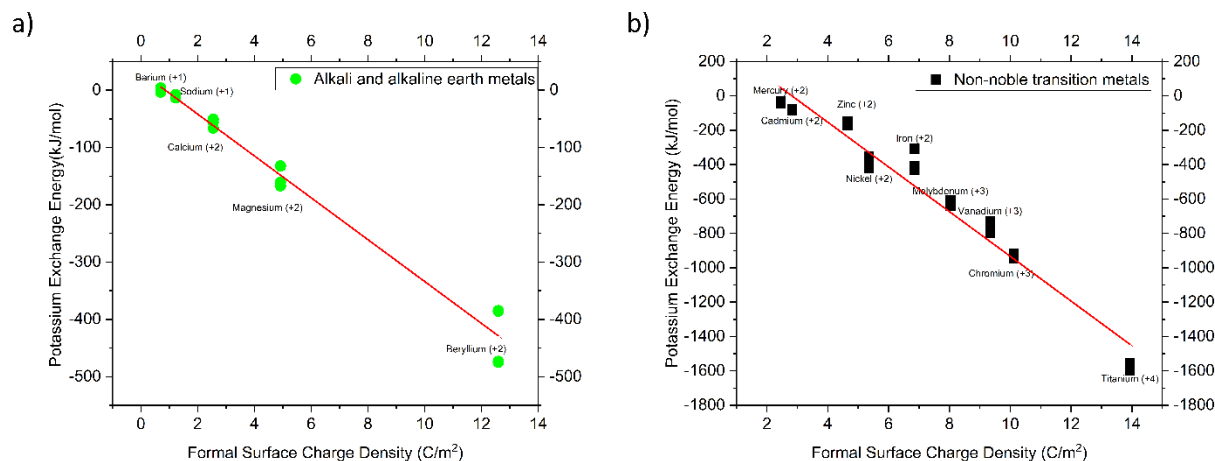


Figure 8. a) Potassium exchange energy plotted against the formal surface charge density for the assessed alkali and alkaline earth metals ($R^2 = 0.98$). b) Potassium exchange energy plotted against the formal surface charge density for the assessed non-noble transition metals ($R^2 = 0.96$).

The logarithm of the negative potassium exchange energy was plotted against the logarithm of the formal surface charge density, and linear regression was performed. These results are presented in Table 9 below. The R^2 values for the noble transition metals group and the post-transition metals and metalloids group increased to 0.89 and 0.77, respectively.

Table 9. Linear regression results for the negative logarithm of the potassium exchange energy versus the logarithm of the formal surface charge density, where the coefficients a and b are based on eq. (15).

Grouping	Alkali and alkaline earth metals	Non-noble transition metals	Noble transition metals	Post-transition metals and metalloids
a	2.1	2.1	4.1	5.8
b	1.70	2.1	1.6	0.63
R^2	0.96	0.96	0.89	0.77

Born Energy

Table 10 presents the coefficients of the linear regression equation and adjusted R^2 values for the potassium exchange energy versus the Born energy. As seen in Table 10, potassium exchange energy is strongly correlated with Born energy for all four groups. This correlation is strongest in the non-noble transition metals group and the noble transition metals group, which have R^2 values of 0.96 and 0.93, respectively. The R^2 values for the Alkali and alkaline earth metals group (0.86) and the post-transition metals and metalloids group (0.79) are also high. Because the Born energy accounts for cation properties as well as the dielectric permittivity of the medium, these results indicate that the potassium exchange energy is strongly predicted by both cation properties and the medium in which adsorption is occurring. Figures 9a and 9b present the graphs of the potassium exchange energy versus the Born energy for non-noble transition metals and noble transition metals, which had the highest R^2 values.

Table 10. Linear regression results for potassium exchange energy versus Born energy, where the coefficients a and b are based on eq. (15).

Grouping	Alkali and alkaline earth metals	Non-noble transition metals	Noble transition metals	Post-transition metals and metalloids
a	70	130	200	-200
b	-5.7	-7.5	-17	-9
R^2	0.86	0.96	0.93	0.79

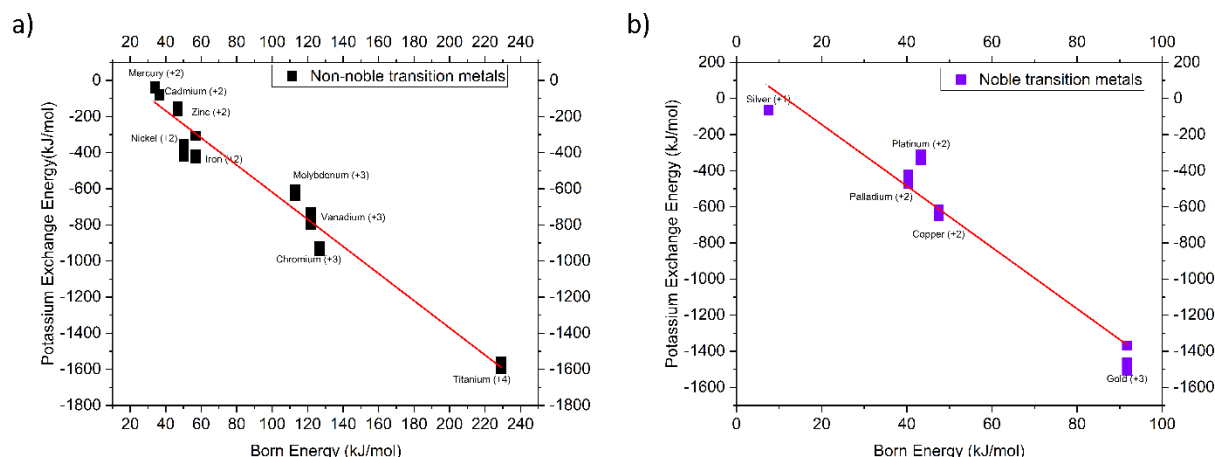


Figure 9. a) Potassium exchange energy plotted against the Born energy for the assessed non-noble transition metals ($R^2 = 0.96$). b) Potassium exchange energy plotted against the Born energy for the assessed noble transition metals ($R^2 = 0.93$).

The logarithm of the negative potassium exchange energy was plotted against the logarithm of the Born energy, and linear regression was performed. These results are presented in Table 11 below. The R^2 value for the post-transition metals and metalloids group increased to 0.90. The R^2 value for the non-noble transition metals group decreased to 0.82.

Table 11. Linear regression results for the negative logarithm of the potassium exchange energy versus the logarithm of the Born energy, where the coefficients a and b are based on eq. (15).

Grouping	Alkali and alkaline earth metals	Non-noble transition metals	Noble transition metals	Post-transition metals and metalloids
a	-1.8	-1.4	1.6	3.0
b	1.77	1.7	1.21	0.88
R^2	0.96	0.82	0.96	0.90

Electric Potential Energy

The linear regression equation coefficients and adjusted R^2 values for the potassium exchange energy versus the electric potential energy are presented in Table 12. As seen in Table 12, potassium exchange energy is strongly correlated with electric potential energy for the non-noble transition metals group ($R^2 = 0.94$). There is also a strong correlation in the post-transition

metals and metalloids group, in which $R^2 = 0.84$, and the noble transition metals group, in which $R^2 = 0.82$. There is a moderate correlation between potassium exchange energy and electric potential energy in the alkali and alkaline earth metals group ($R^2 = 0.65$). The electric potential energy is calculated based on the cation properties (charge and radius), the medium (dielectric permittivity), and the anion properties (charge and radius). Therefore, these results indicate that potassium exchange energy can be strongly predicted based on cation, anion, and medium-associated properties for non-noble and noble transition metals, as well as post-transition metals and metalloids. Figures 10a and 10b present the graphs of the potassium exchange energy versus the electric potential energy for the non-noble transition metals group and the post-transition metals and metalloids group, which had the highest R^2 values.

Table 12. Linear regression results for potassium exchange energy versus electric potential energy, where the coefficients a and b are based on eq. (15).

Grouping	Alkali and alkaline earth metals	Non-noble transition metals	Noble transition metals	Post-transition metals and metalloids
a	200	910	700	700
b	13	35	42	40
R^2	0.65	0.94	0.82	0.84

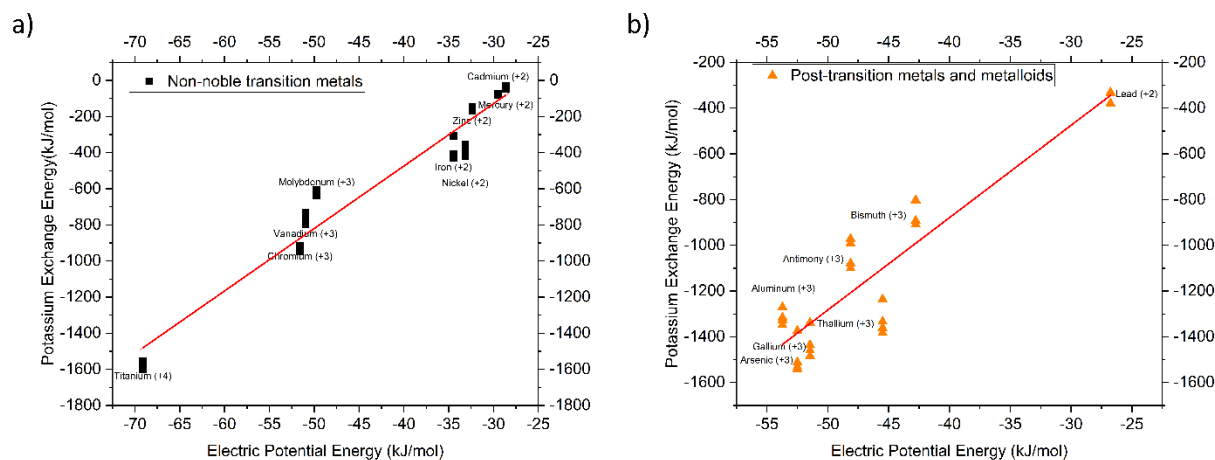


Figure 10. a) Potassium exchange energy plotted against the electric potential energy for the assessed non-noble transition metals ($R^2 = 0.94$). b) Potassium exchange energy plotted against the electric potential for the assessed post-transition metals and metalloids ($R^2 = 0.84$).

The logarithm of the negative potassium exchange energy was plotted against the logarithm of the negative electric potential energy, and linear regression was performed. These results are presented in Table 13 below. The R^2 values for the alkali and alkaline earth metals, noble transition metals, and post-transition metals and metalloids groups are greater than 0.90. This indicates that there is a very strong correlation between the potassium exchange energy and the electric potential energy. However, as with the case of the logarithm of the Born energy (Table 11), the R^2 value for the non-noble transition metals group decreased ($R^2 = 0.78$).

Table 13. Linear regression results for the negative logarithm of the potassium exchange energy versus the negative logarithm of the electric potential energy, where the coefficients a and b are based on eq. (15).

Grouping	Alkali and alkaline earth metals	Non-noble transition metals	Noble transition metals	Post-transition metals and metalloids
a	-8.2	-7	-2.4	-0.8
b	3.8	3.5	2.5	2.0
R^2	0.93	0.78	0.96	0.92

Conclusions and Recommendations for Future Work

Based on the DFT simulations comparing copper (II) and lead (II), it was found that binding sites containing acidic hydrogen are more favorable than binding sites that did not contain acidic hydrogen. Specifically, binding sites in which the metal cation complexed with either hydroxyl or carboxyl groups have more negative potassium exchange energies. It was also found that copper (II) has more negative potassium exchange energies than lead (II), which suggests that the modeled hydrothermal char should have a higher adsorption capacity for copper (II) than for lead (II). However, due to limitations in modeling accuracy with DFT simulations, it is important that this trend is validated experimentally. This can be accomplished with the proposed methodology for determining the adsorption capacities for copper (II) and lead (II) in a competitive adsorption experiment.

It was found that the potassium exchange energies are much more negative than experimentally determined adsorption energies. This could be due to the inability of DFT to accurately capture the effects of Van der Waals forces, which have a crucial role in adsorption in an aqueous environment due to hydrogen bonding. To incorporate the effects of hydrogen bonding into the model, it is likely necessary that explicit water molecules must be added to the simulation. When modeling explicit water solvation, however, it was found that the potassium exchange energies became more negative as water was added to the simulation. This indicated that explicit water solvation was modeled inaccurately in this work. Instead, it may be more accurate to model the effects of water solvation by modeling the solvation shell of the metal cation, which is the set of water molecules that interacts with the metal via hydrogen bonding. By properly modeling the solvation shell, the calculated potassium exchange energies may be closer to experimentally obtained adsorption energies.

Based on the results from the linear fitting of physical properties, potassium exchange energy is strongly correlated to formal surface charge density, Born energy, and electric potential energy. The assessed metals were divided into groupings based on the periodic table and had unique coefficients for each group. Therefore, this set of properties could be used to predict potassium exchange energies of various metals using the calculated coefficients of the linear regression curves.

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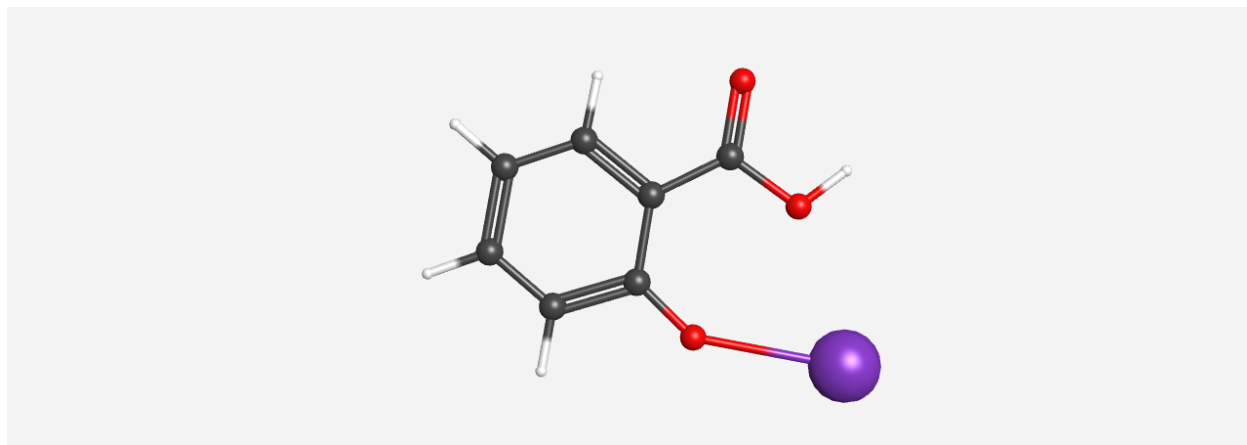
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Appendices

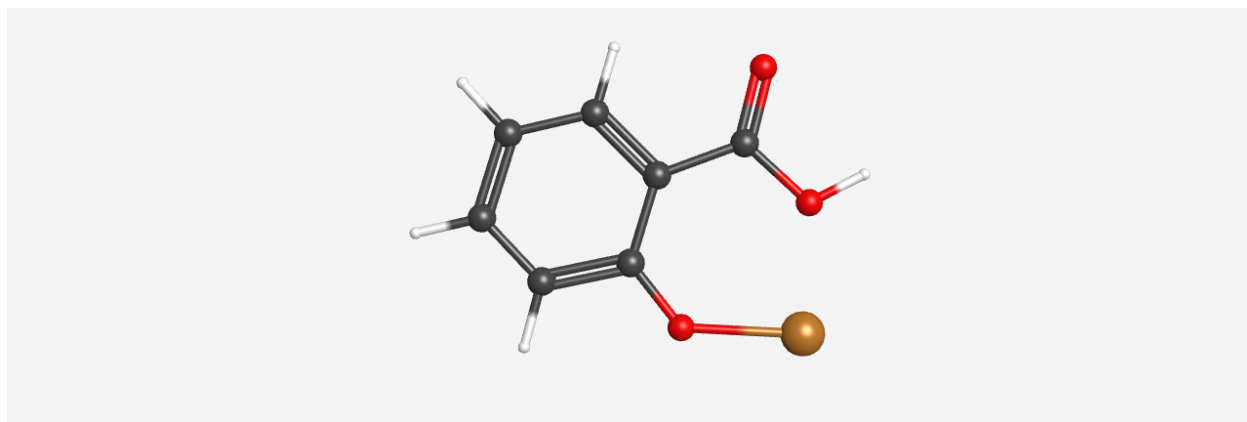
Appendix A: Binding Site Geometries

Binding Site 1A

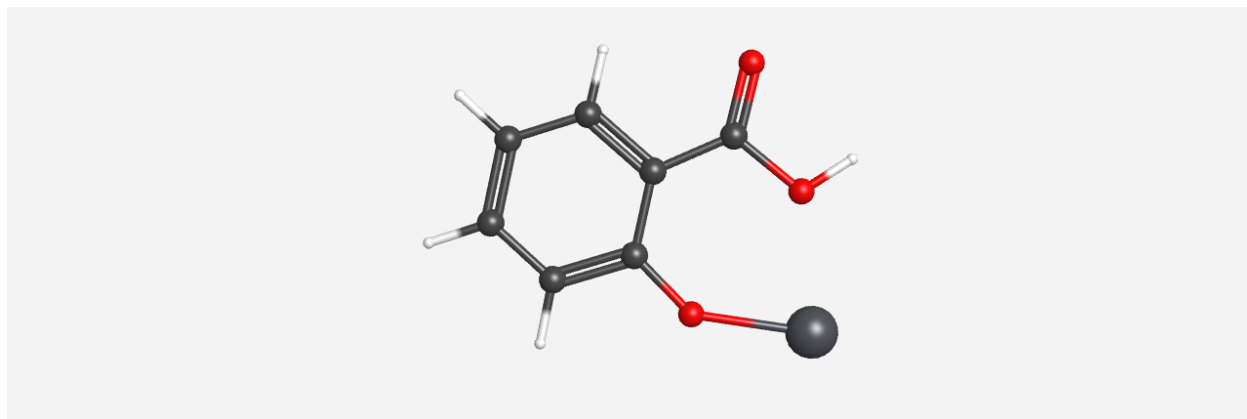
Reactant geometry:



Cu(II) product geometry:

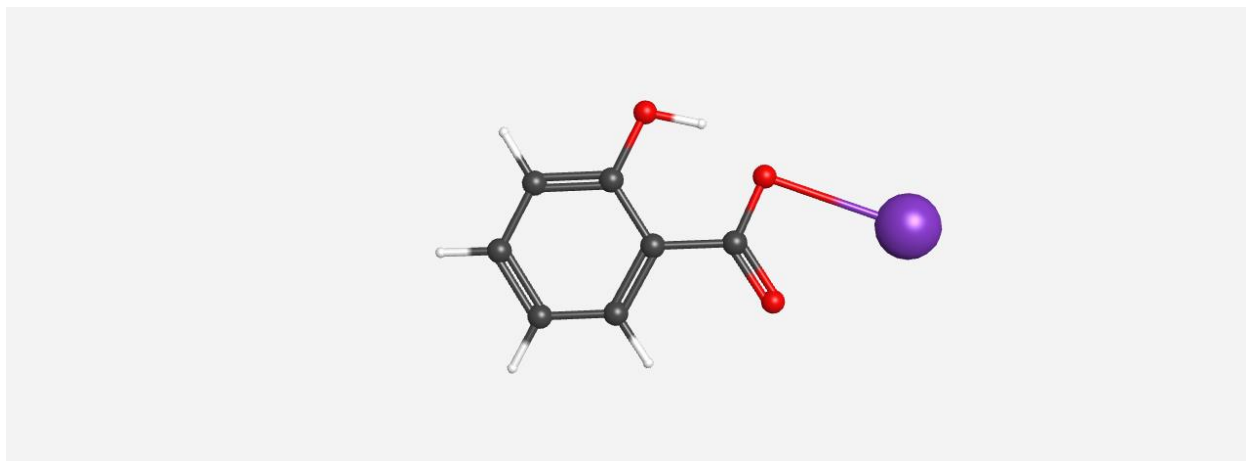


Pb(II) product geometry:

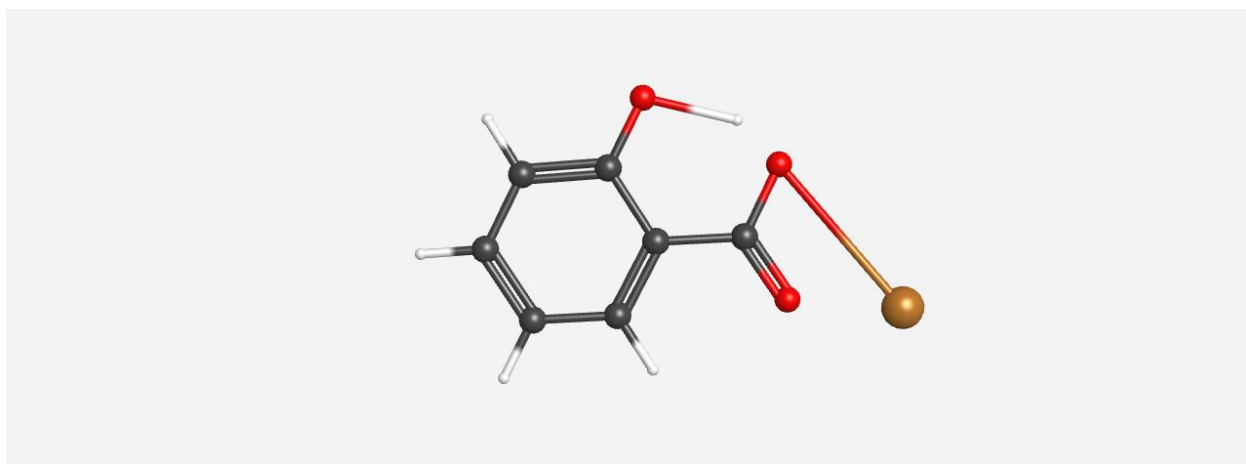


Binding Site 1B

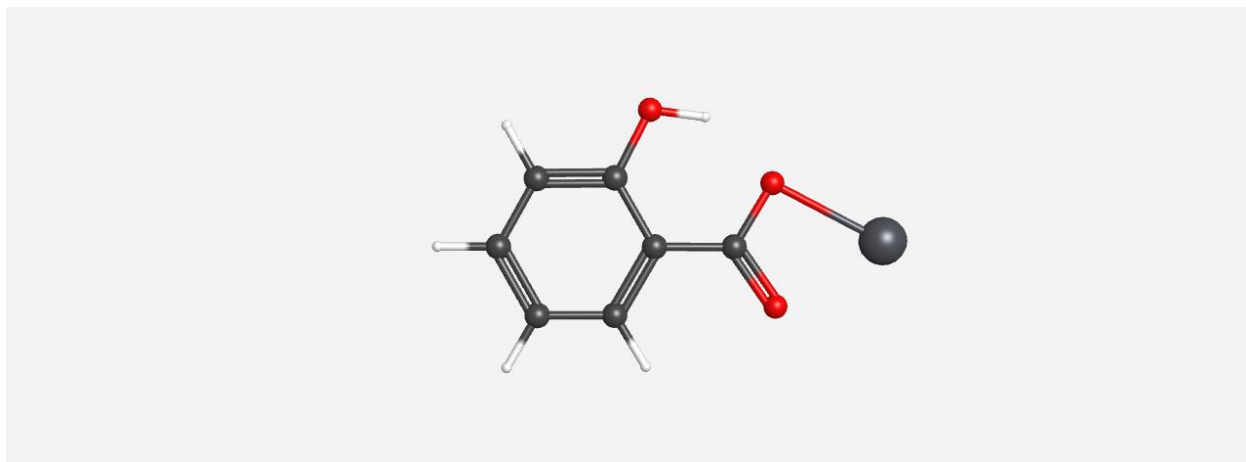
Reactant geometry:



Cu(II) product geometry:



Pb(II) product geometry:



Binding Site 2

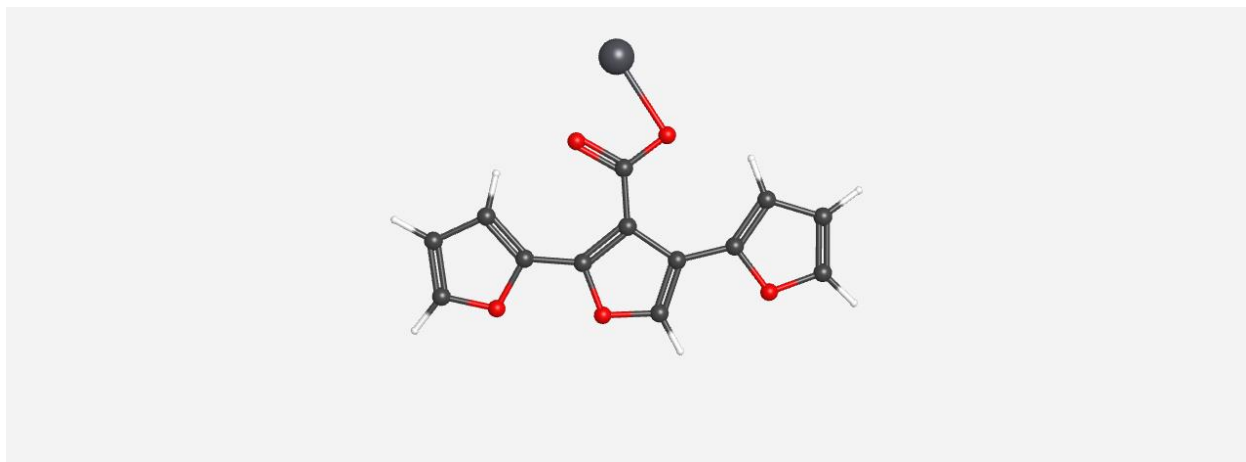
Reactant geometry:



Cu(II) product geometry:



Pb(II) product geometry:

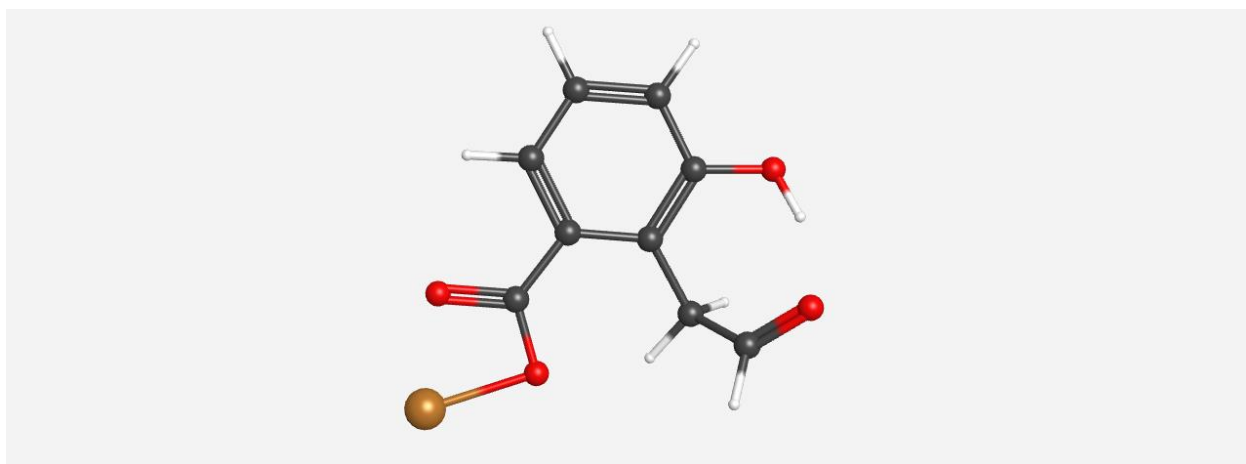


Binding Site 3A

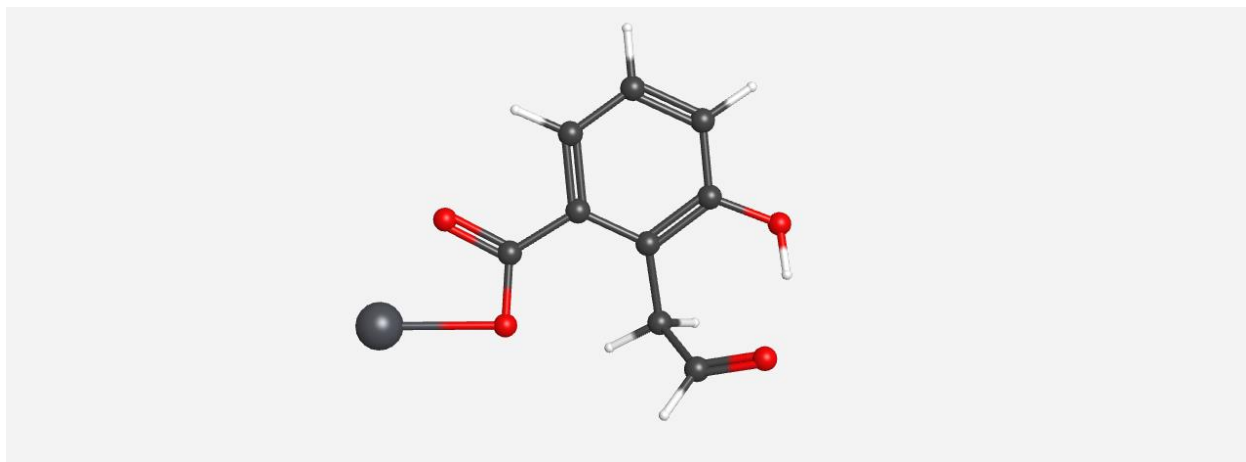
Reactant geometry:



Cu(II) product geometry:



Pb(II) product geometry:



Binding Site 3B

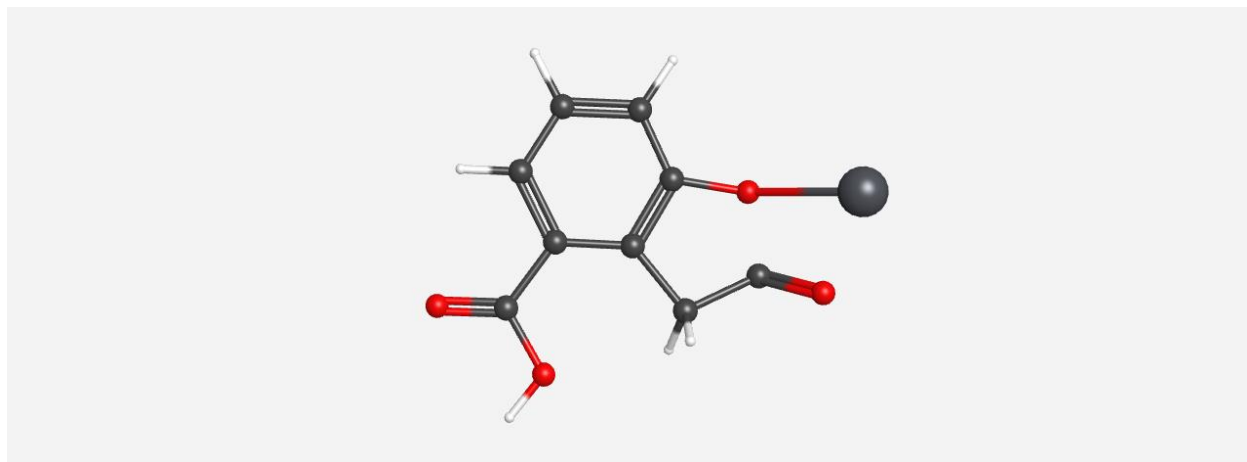
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Cu(II) product geometry:

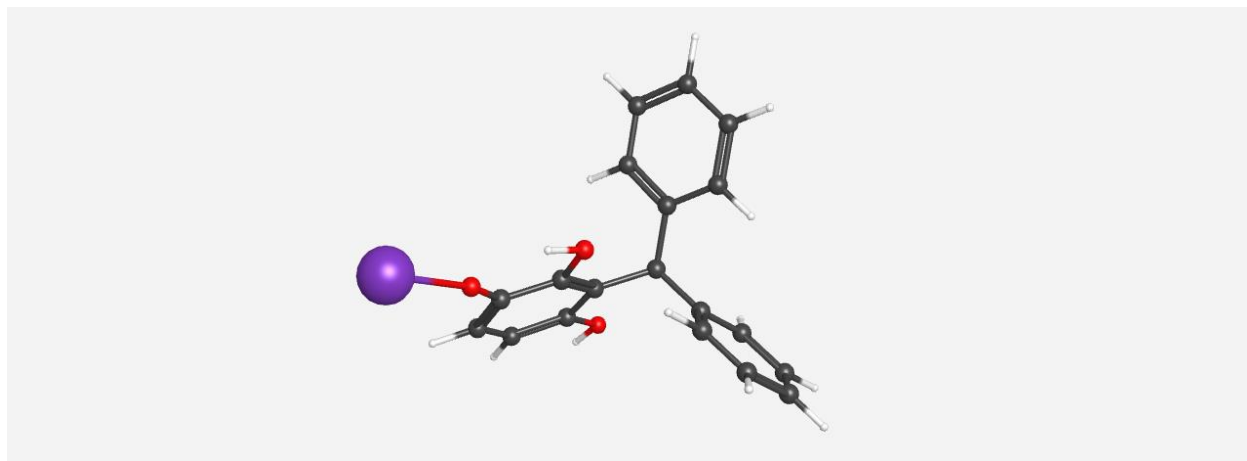


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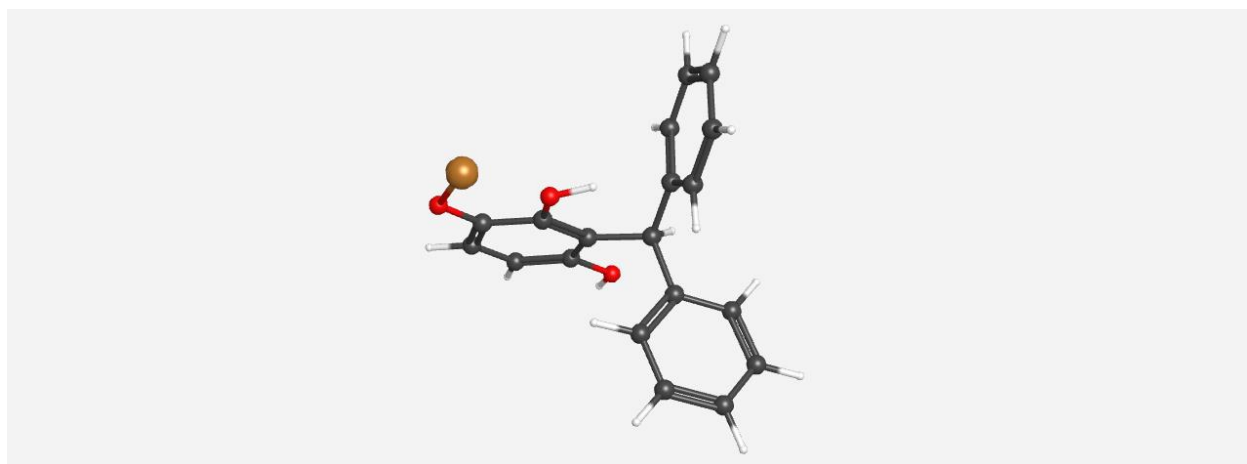


Binding Site 4A

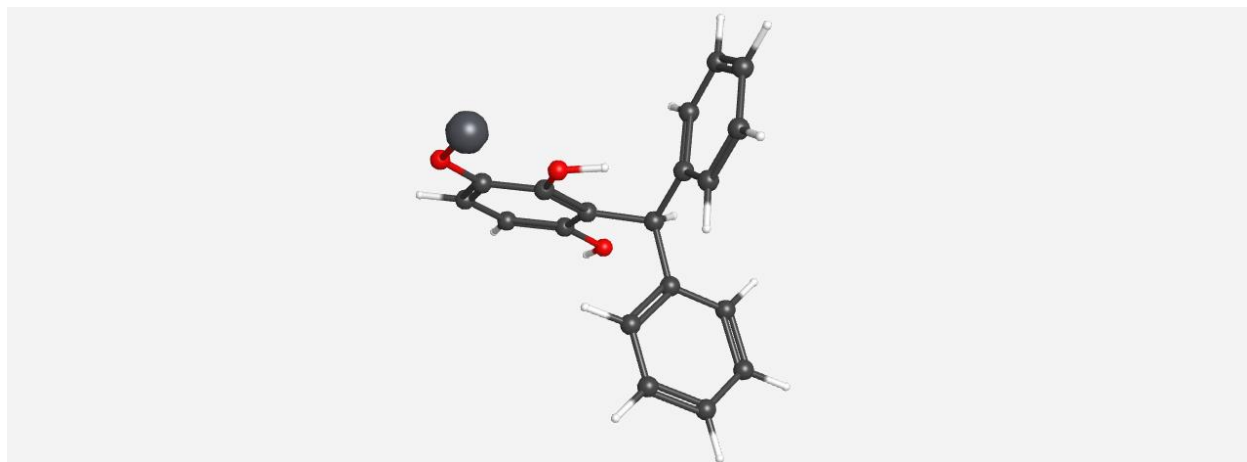
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Cu(II) product geometry:

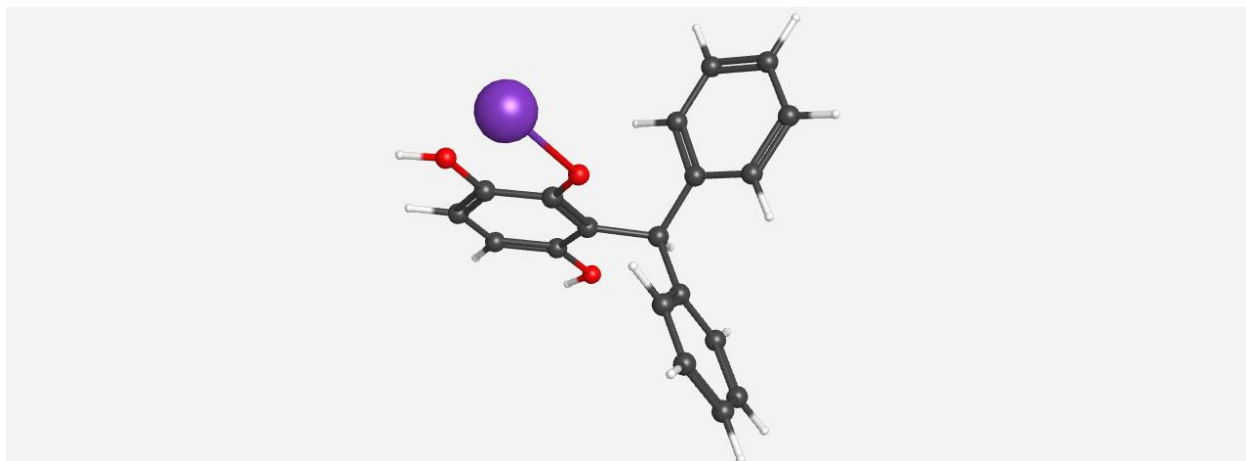


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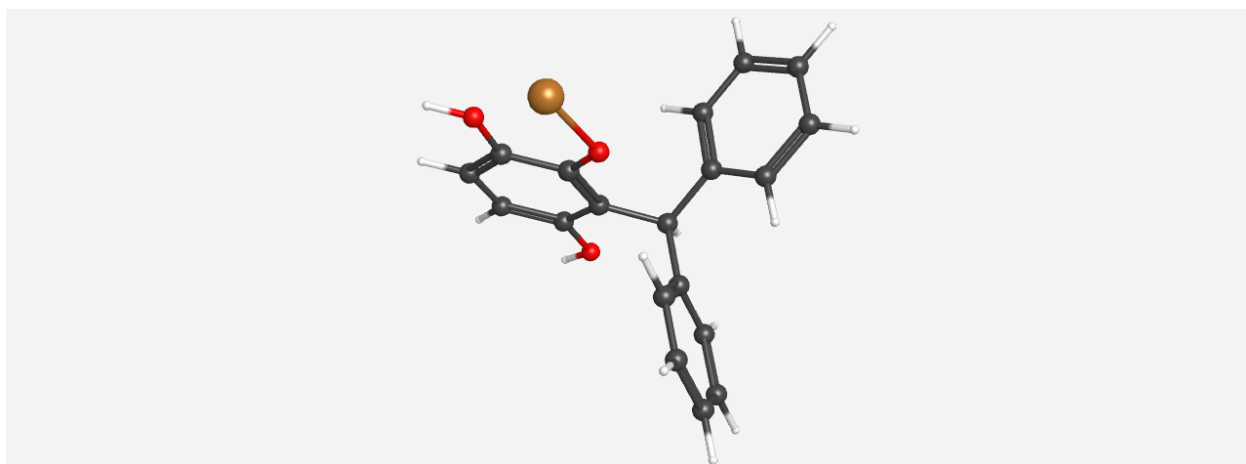


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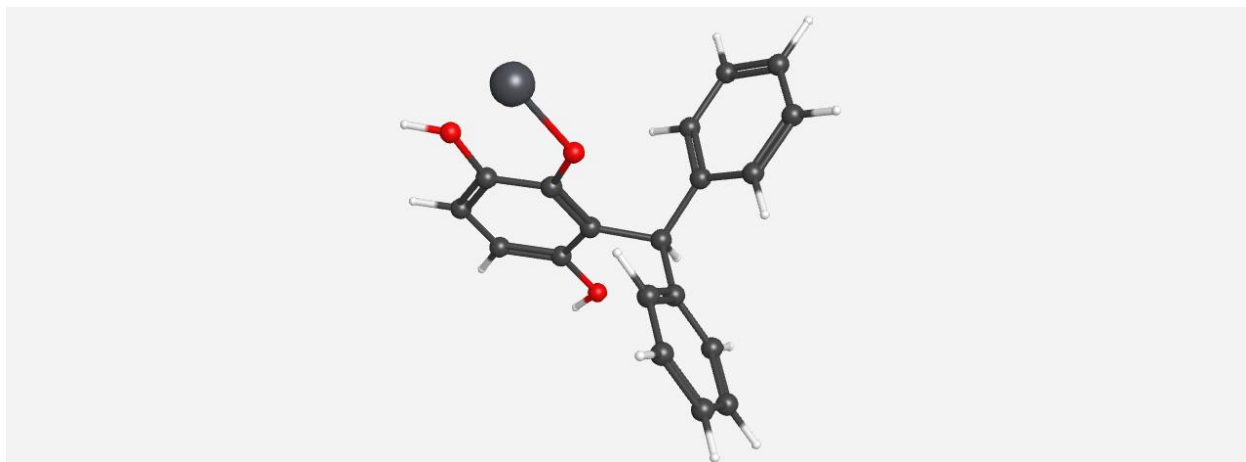
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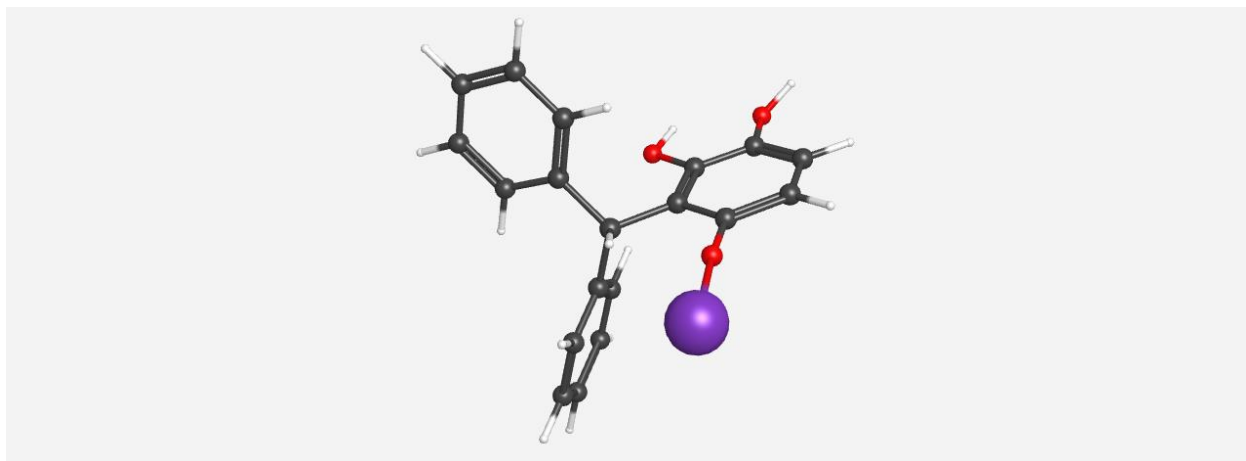


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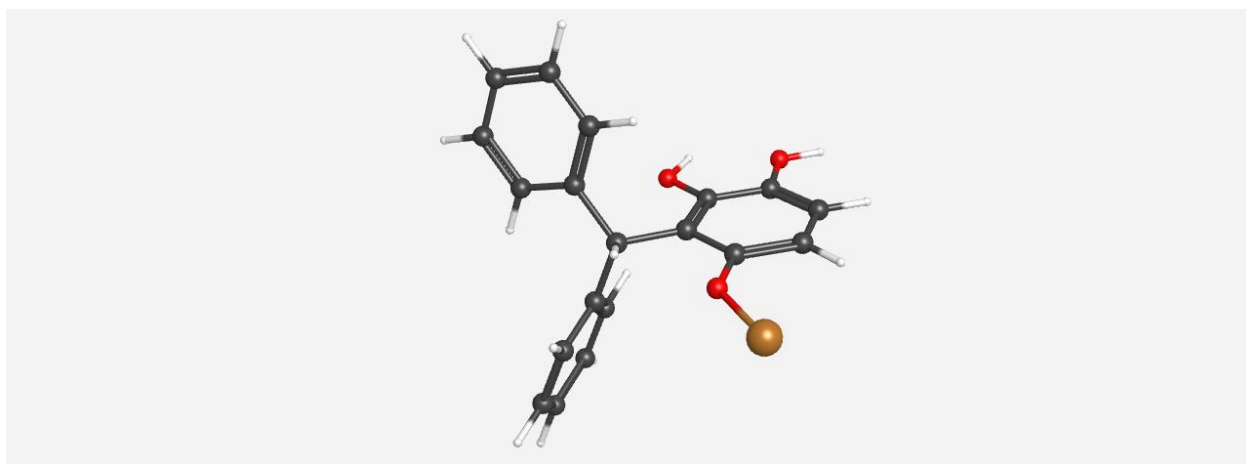


Binding Site 4C

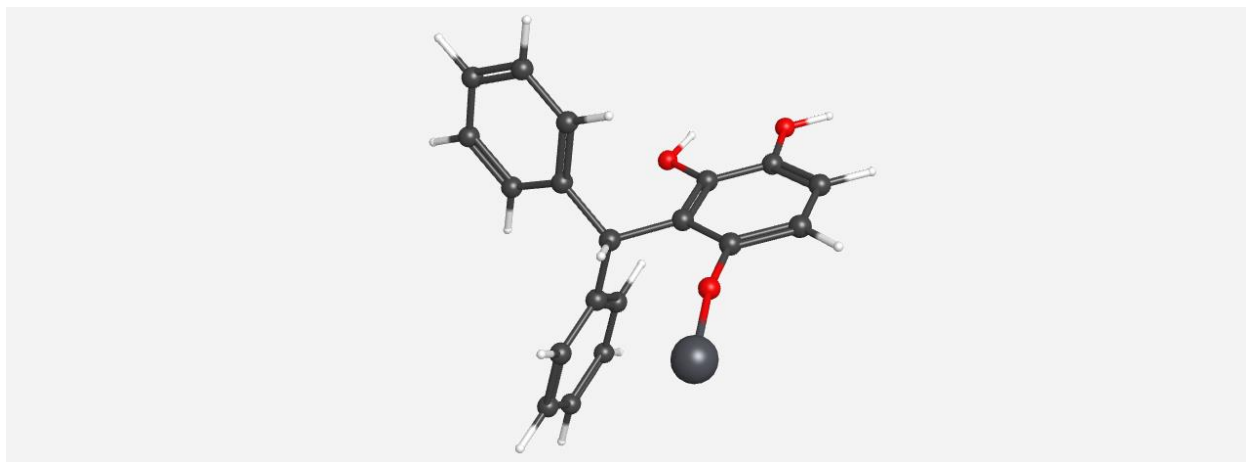
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Cu(II) product geometry:

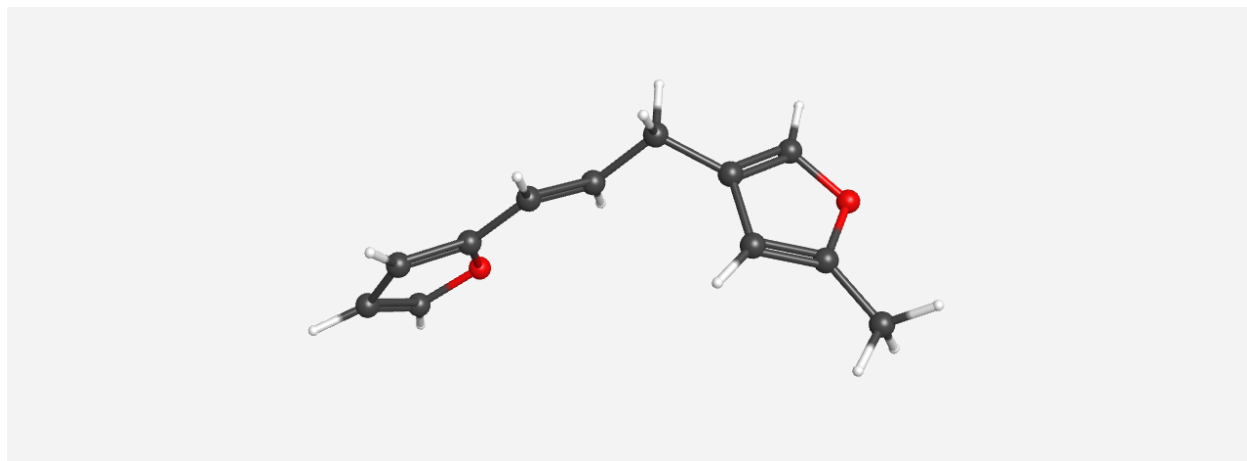


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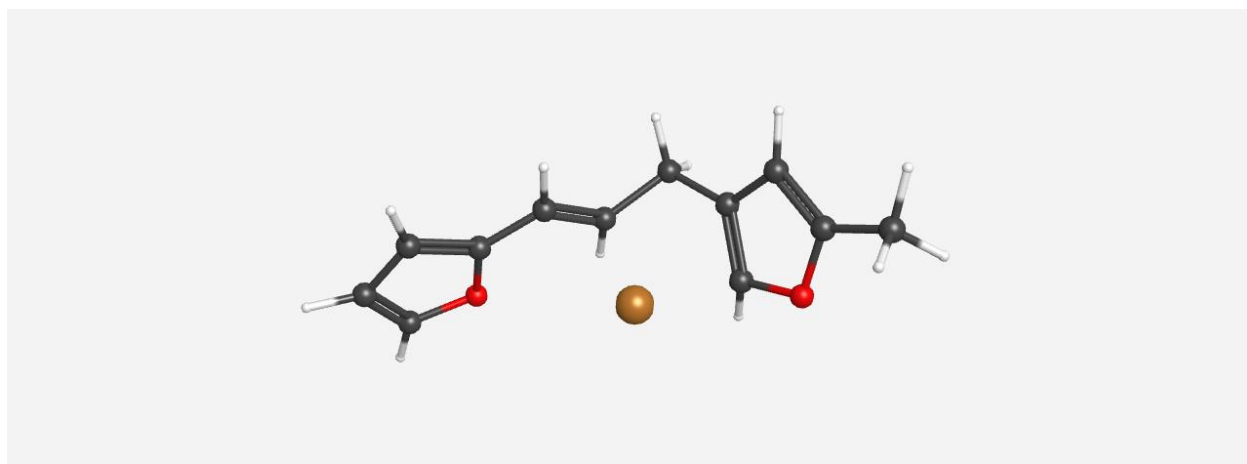


Binding Site 5

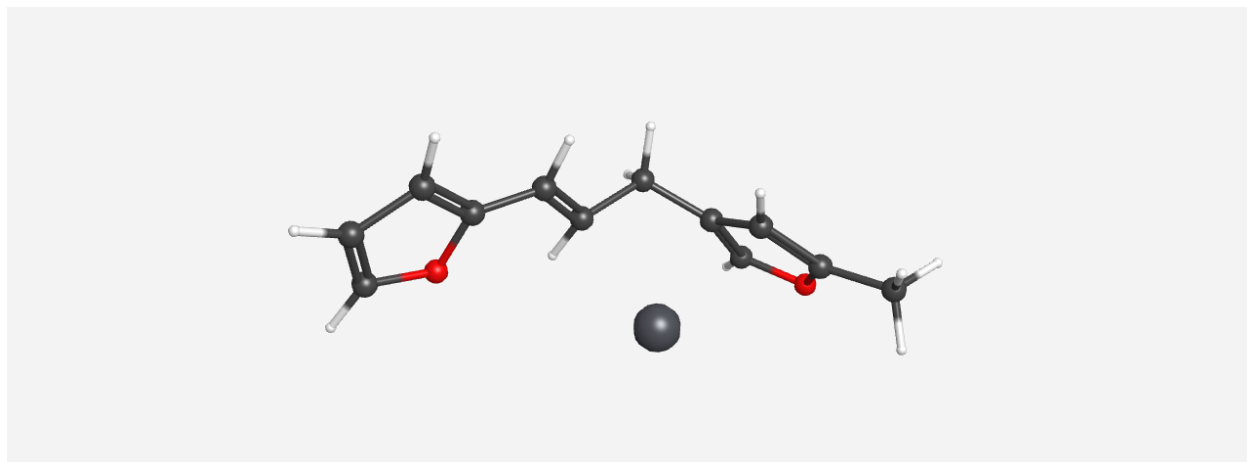
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Cu(II) product geometry:

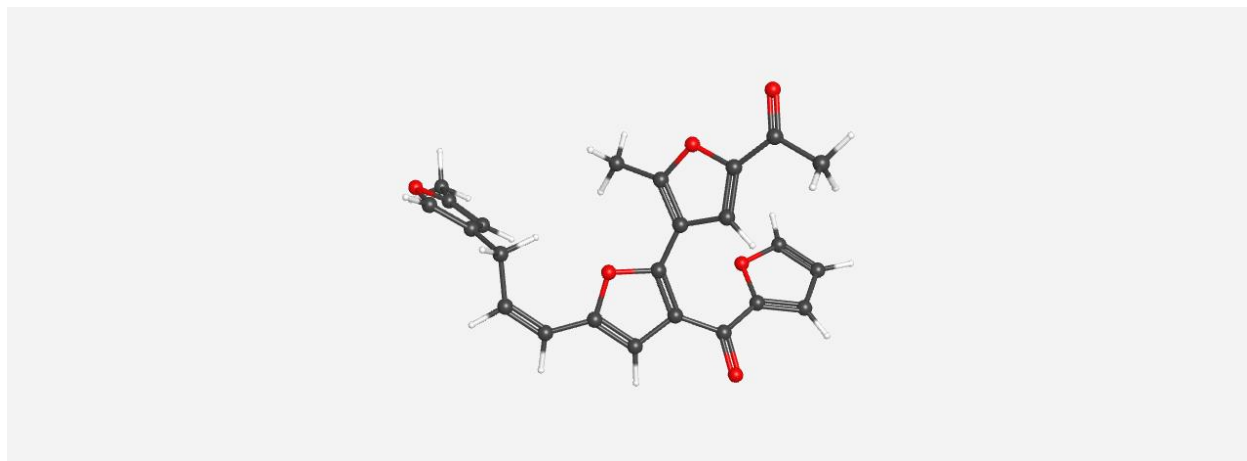


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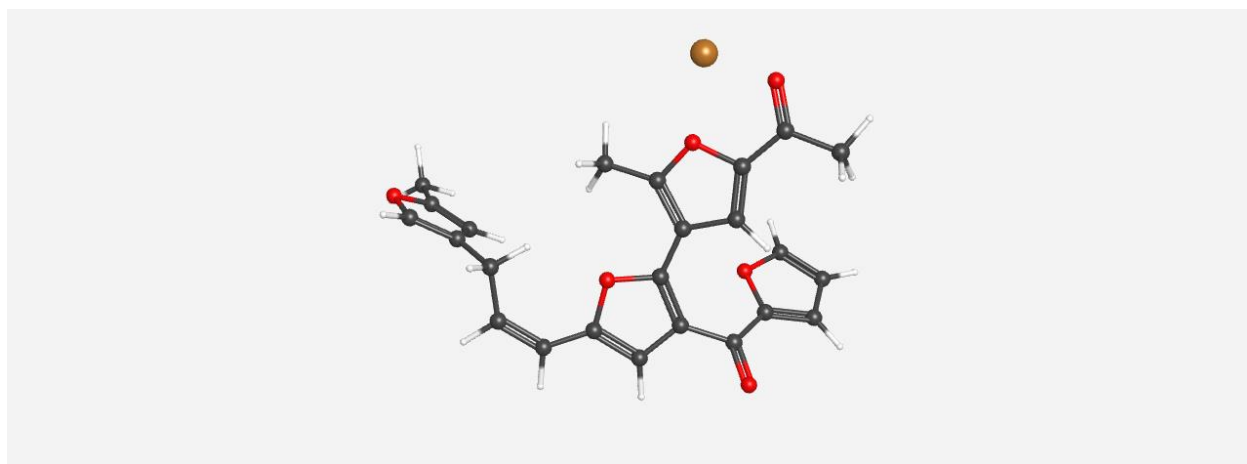


Binding Site 6

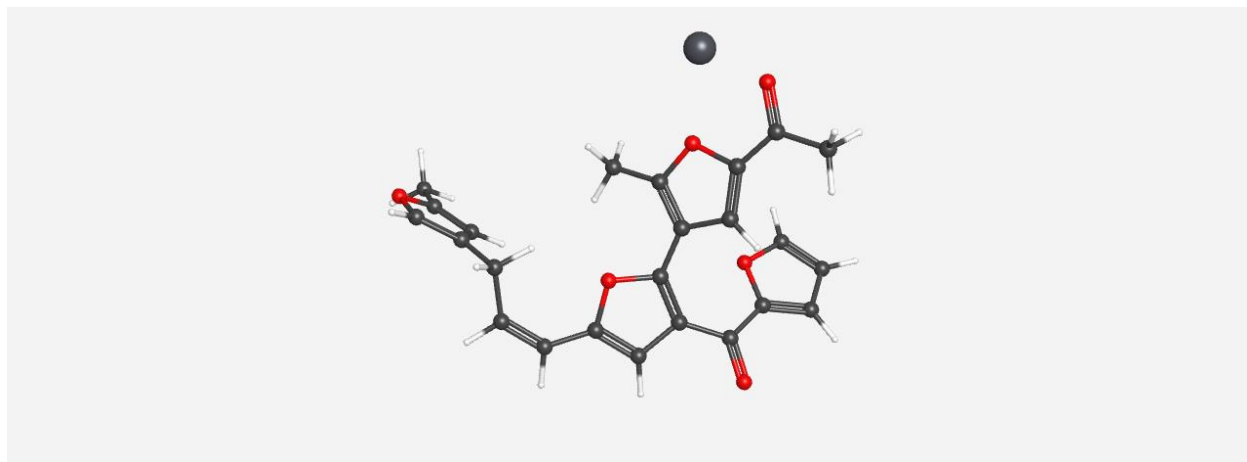
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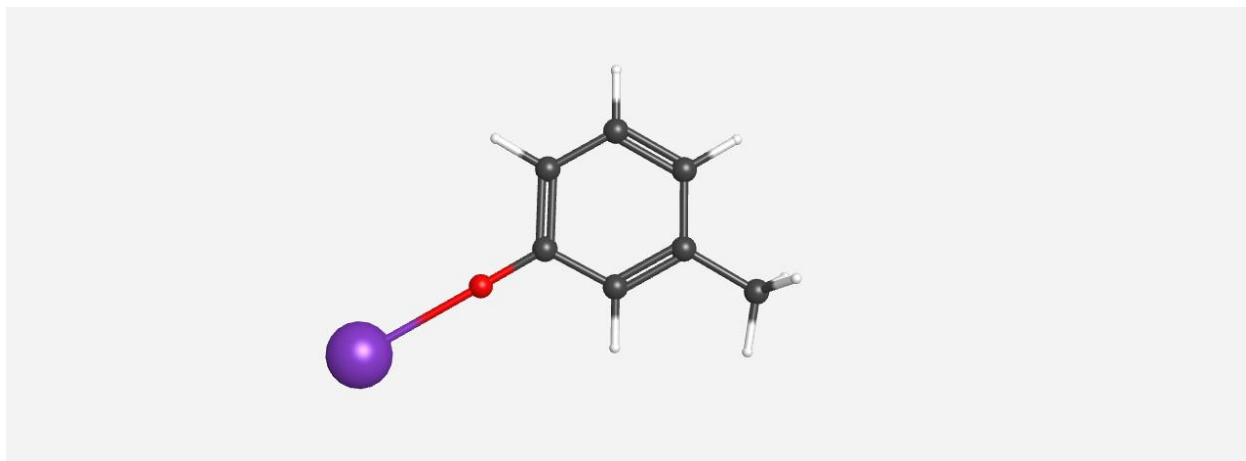


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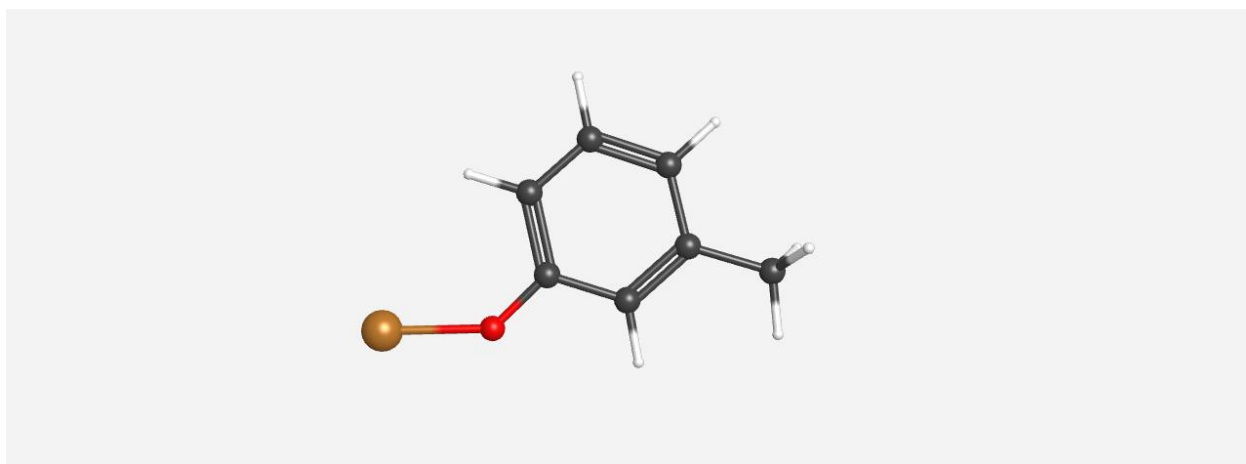


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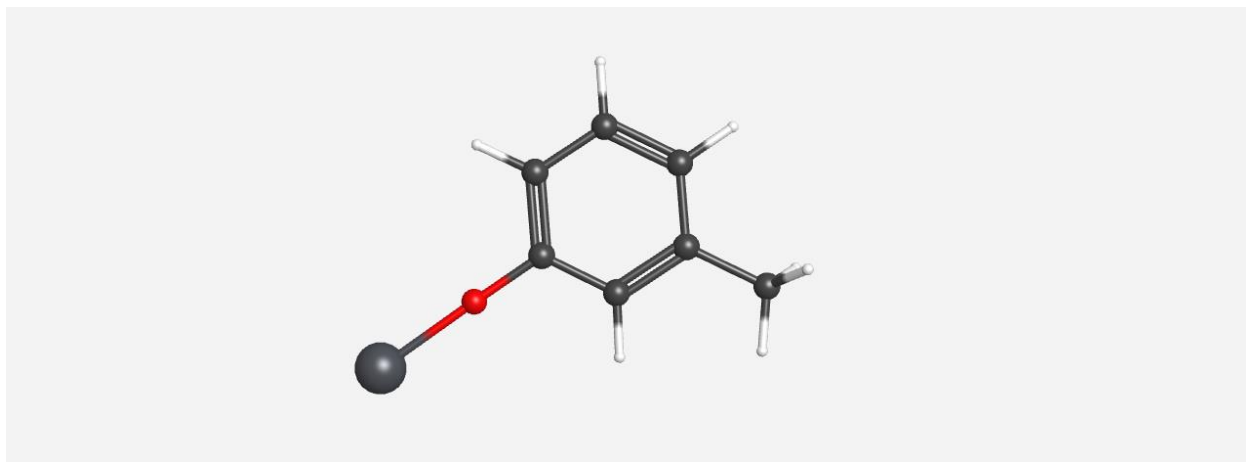
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Cu(II) product geometry:



Pb(II) product geometry:

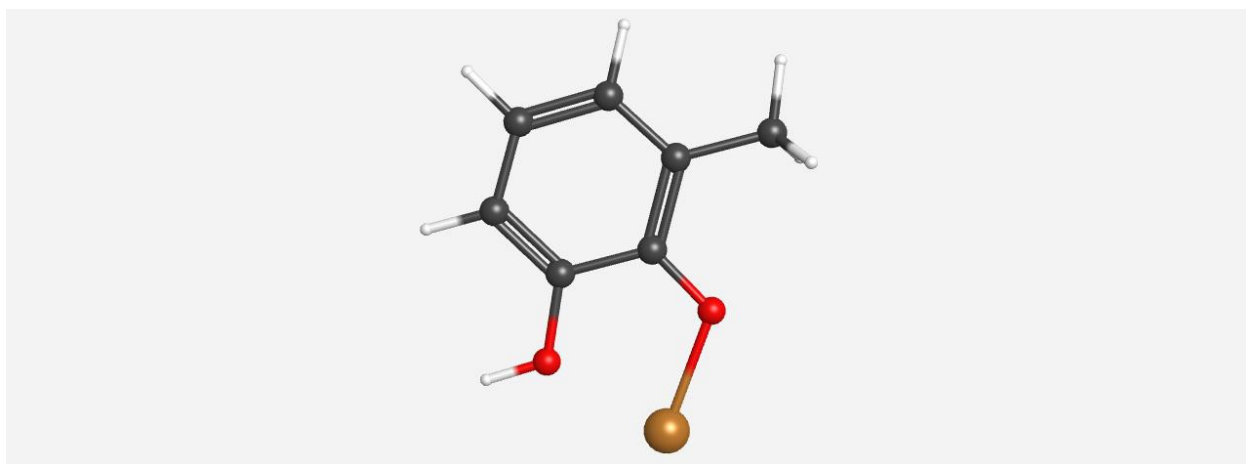


Binding Site 8A

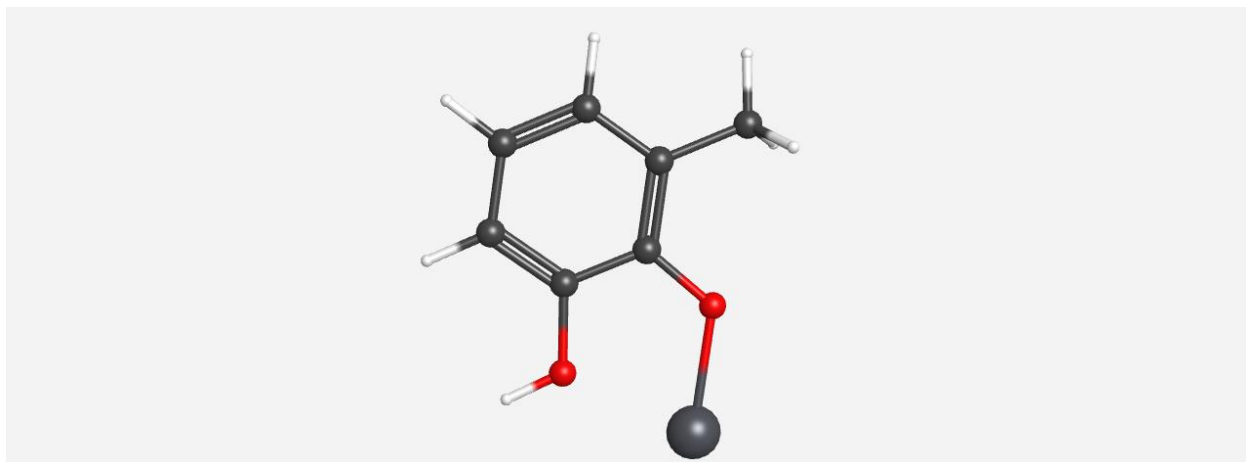
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Cu(II) product geometry:

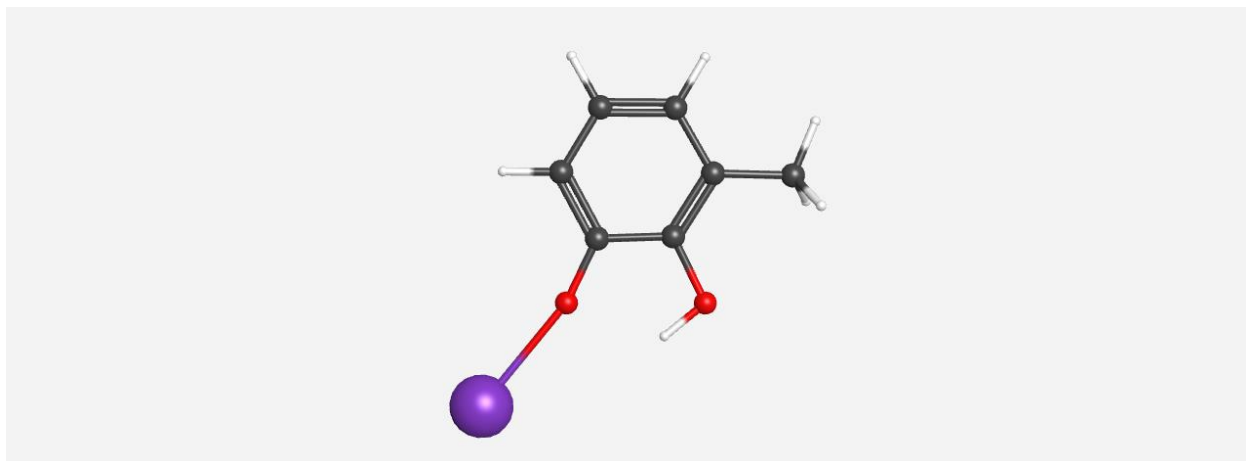


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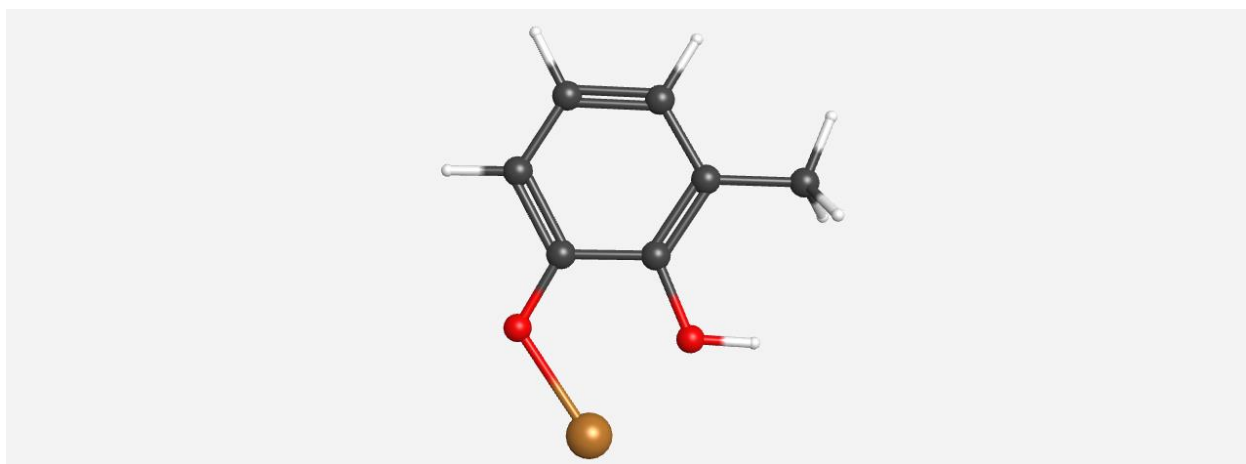


Binding Site 8B

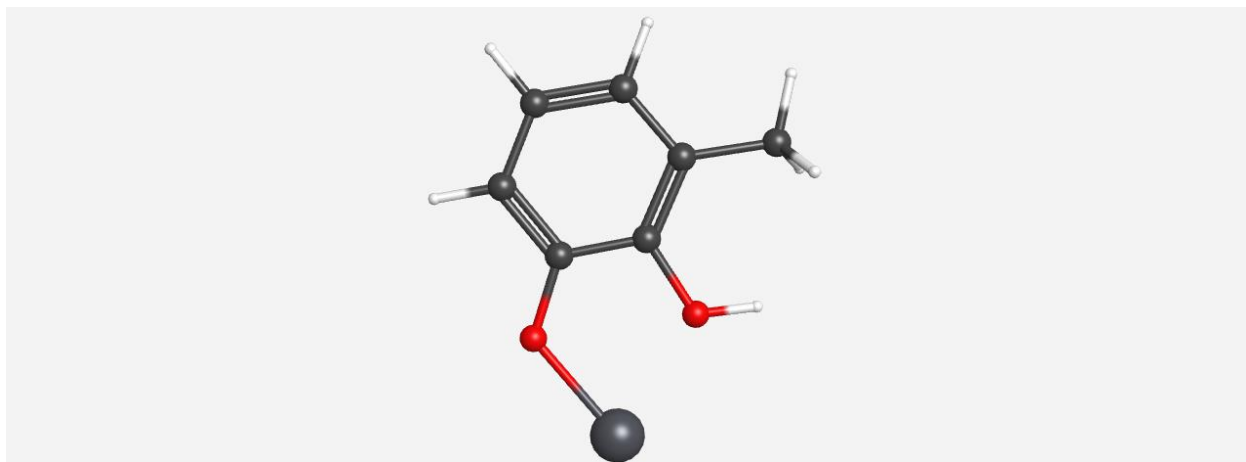
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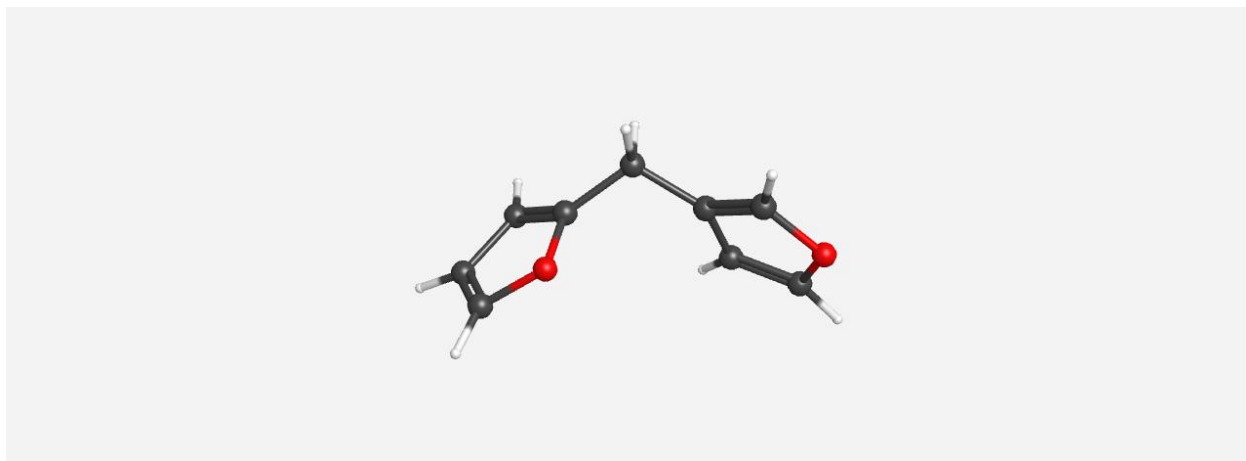


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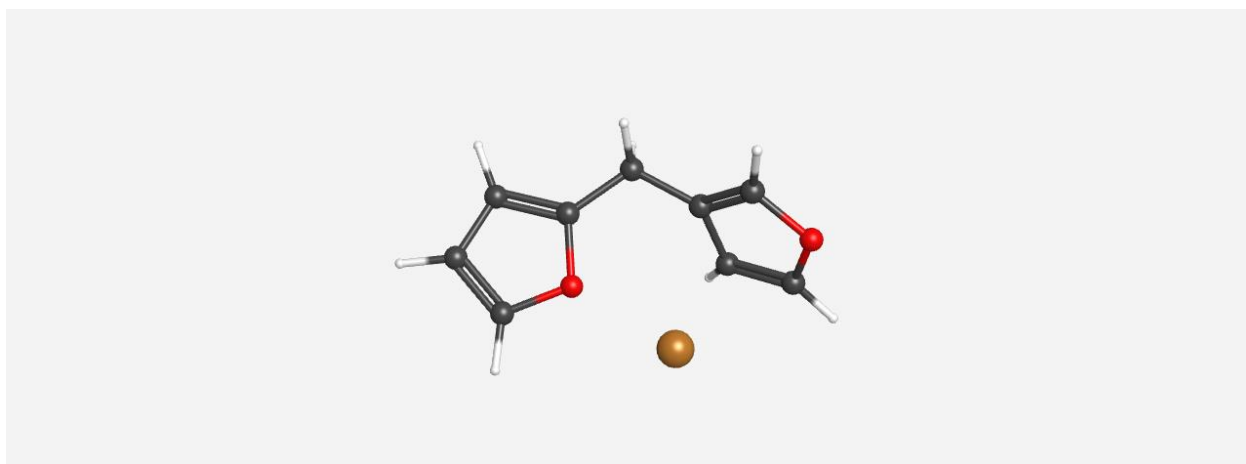


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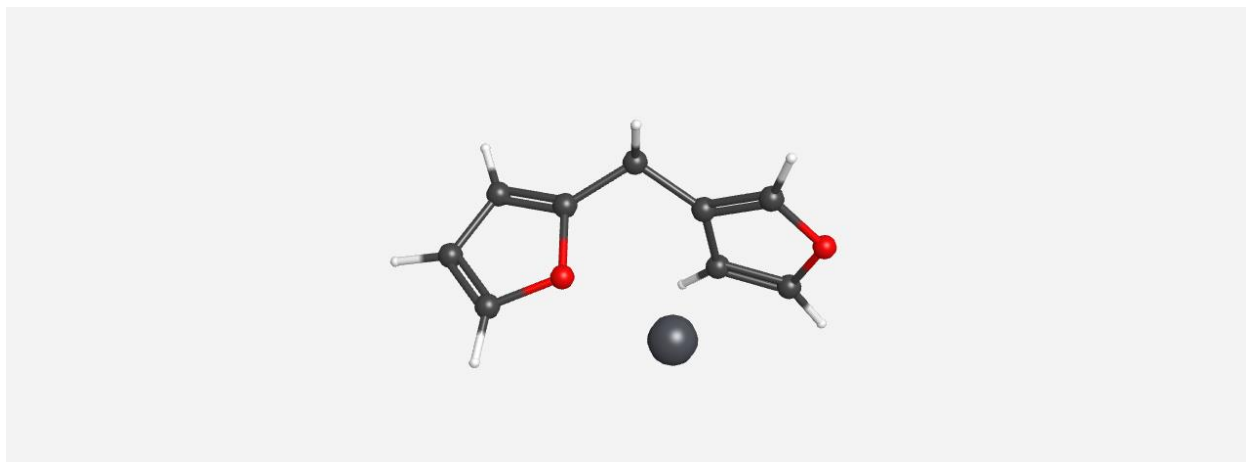
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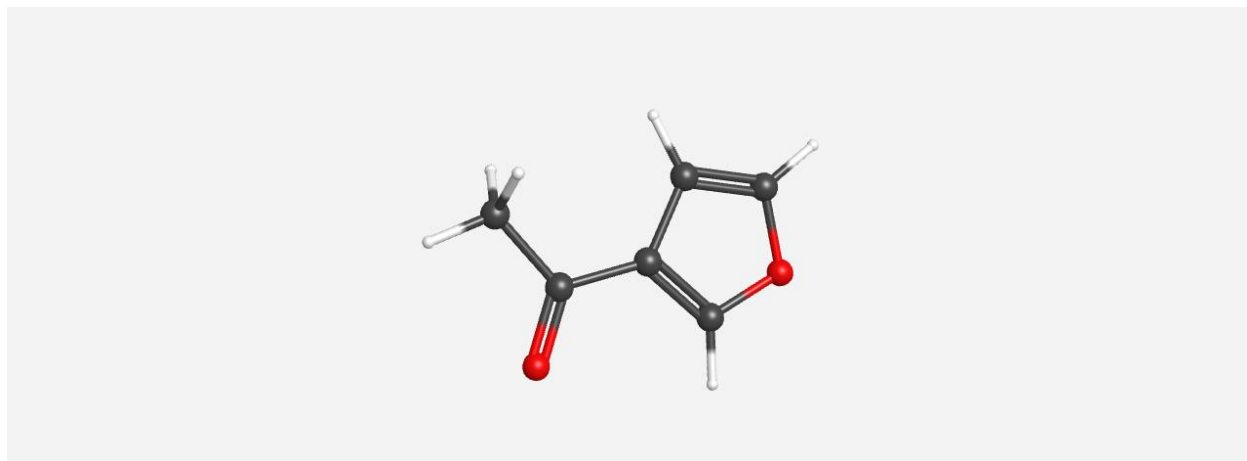


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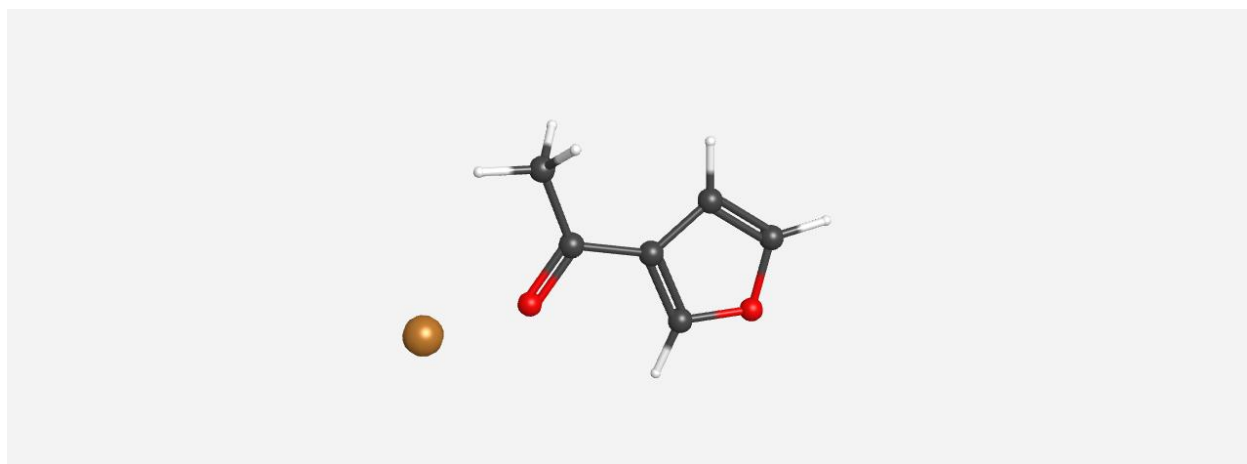


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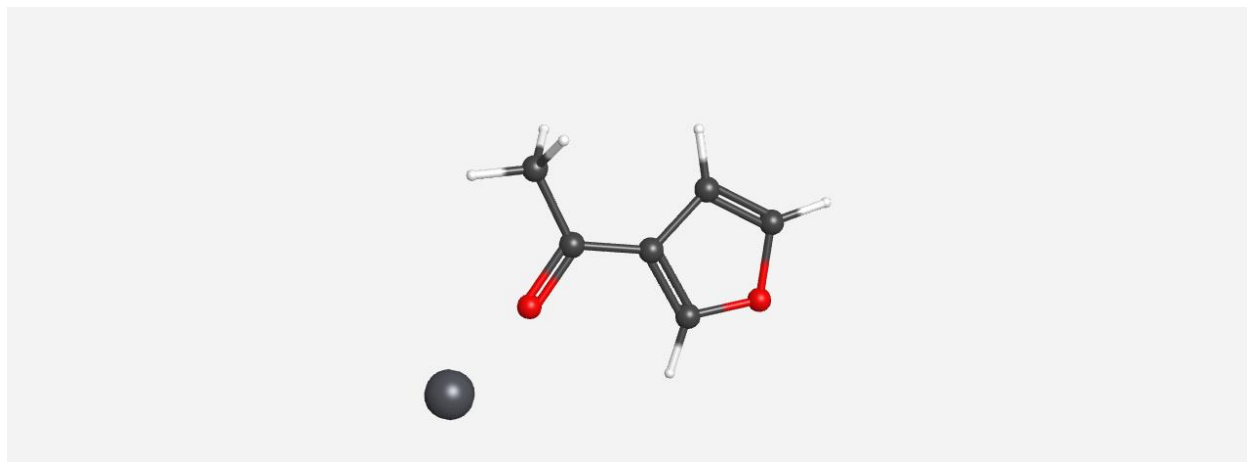
Reactant geometry:



Cu(II) product geometry:



Pb(II) product geometry:



Appendix B: Potassium Exchange Energy Sample Calculations

Binding Site 4A Sample Calculations

$$\text{Potassium exchange energy} = E_{\text{products}} - E_{\text{reactants}} = [(E_{\text{MBS}} + E_{\text{K}^+}) - (E_{\text{BS}} + E_{\text{MC}})]$$

Cu(II):

$$\text{Potassium exchange energy} = E_{\text{products}} - E_{\text{reactants}} = [(E_{\text{MBS}} + E_{\text{K}^+}) - (E_{\text{BS}} + E_{\text{MC}})]$$

$$E_{\text{BS}} = -986.836101457 \text{ Ha}$$

$$E_{\text{MC}} = -195.608877521 \text{ Ha}$$

$$E_{\text{MBS}} = -1154.59826073 \text{ Ha}$$

$$E_{\text{K}^+} = -28.095491411 \text{ Ha}$$

Potassium exchange energy

$$= [(-1154.59826073 \text{ Ha} + -28.095491411 \text{ Ha})$$

$$- (-986.836101457 \text{ Ha} + -195.608877521 \text{ Ha})] \times \frac{2625.5 \frac{\text{kJ}}{\text{mol}}}{\text{Ha}}$$

$$= -653.15 \frac{\text{kJ}}{\text{mol}}$$

Cu(II), One Water Molecule:

$$\text{Potassium exchange energy} = E_{\text{products}} - E_{\text{reactants}} = [(E_{\text{MBS}} + E_{\text{K}^+}) - (E_{\text{BS}} + E_{\text{MC}})]$$

$$E_{\text{BS}} = -1063.27045236 \text{ Ha}$$

$$E_{\text{MC}} = -195.608877521 \text{ Ha}$$

$$E_{\text{MBS}} = -1231.06915083 \text{ Ha}$$

$$E_{\text{K}^+} = -28.095491411 \text{ Ha}$$

Potassium exchange energy

$$= [(-1231.06915083 \text{ Ha} + -28.095491411 \text{ Ha})$$

$$- (-1063.27045236 \text{ Ha} + -195.608877521 \text{ Ha})] \times \frac{2625.5 \frac{\text{kJ}}{\text{mol}}}{\text{Ha}}$$

$$= -749.09 \frac{\text{kJ}}{\text{mol}}$$

Cu(II), Two Water Molecules:

$$\text{Potassium exchange energy} = E_{\text{products}} - E_{\text{reactants}} = [(E_{\text{MBS}} + E_{\text{K}^+}) - (E_{\text{BS}} + E_{\text{MC}})]$$

$$E_{\text{BS}} = -1139.71627736 \text{ Ha}$$

$$E_{\text{MC}} = -195.608877521 \text{ Ha}$$

$$E_{\text{MBS}} = -1307.51391802 \text{ Ha}$$

$$E_{\text{K}^+} = -28.095491411 \text{ Ha}$$

Potassium exchange energy

$$= [(-1307.51391802 \text{ Ha} + -28.095491411 \text{ Ha})$$

$$- (-1139.71627736 \text{ Ha} + -195.608877521 \text{ Ha})] \times \frac{2625.5 \frac{\text{kJ}}{\text{mol}}}{\text{Ha}}$$

$$= -746.31 \frac{\text{kJ}}{\text{mol}}$$

Pb(II):

$$\text{Potassium exchange energy} = E_{\text{products}} - E_{\text{reactants}} = [(E_{\text{MBS}} + E_{\text{K}^+}) - (E_{\text{BS}} + E_{\text{MC}})]$$

$$E_{\text{BS}} = -986.836101457 \text{ Ha}$$

$$E_{\text{MC}} = -3.097986909 \text{ Ha}$$

$$E_{\text{MBS}} = -961.982847252 \text{ Ha}$$

$$E_{\text{K}^+} = -28.095491411 \text{ Ha}$$

Potassium exchange energy

$$= [(-961.982847252 \text{ Ha} + -28.095491411 \text{ Ha})$$

$$- (-986.836101457 \text{ Ha} + -3.097986909 \text{ Ha})] \times \frac{2625.5 \frac{\text{kJ}}{\text{mol}}}{\text{Ha}}$$

$$= -378.73 \frac{\text{kJ}}{\text{mol}}$$

Pb(II), One Water Molecule:

$$\text{Potassium exchange energy} = E_{\text{products}} - E_{\text{reactants}} = [(E_{\text{MBS}} + E_{\text{K}^+}) - (E_{\text{BS}} + E_{\text{MC}})]$$

$$E_{\text{BS}} = -1063.27045236 \text{ Ha}$$

$$E_{\text{MC}} = -3.097986909 \text{ Ha}$$

$$E_{MBS} = -1038.41865991 \text{ Ha}$$

$$E_{K+} = -28.095491411 \text{ Ha}$$

Potassium exchange energy

$$\begin{aligned} &= [(-1038.41865991 \text{ Ha} + -28.095491411 \text{ Ha}) \\ &\quad - (-1063.27045236 \text{ Ha} + -3.097986909 \text{ Ha})] \times \frac{2625.5 \frac{\text{kJ}}{\text{mol}}}{\text{Ha}} \\ &= -382.57 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

Pb(II), Two Water Molecules:

$$\text{Potassium exchange energy} = E_{\text{products}} - E_{\text{reactants}} = [(E_{MBS} + E_{K+}) - (E_{BS} + E_{MC})]$$

$$E_{BS} = -1139.71627736 \text{ Ha}$$

$$E_{MC} = -3.097986909 \text{ Ha}$$

$$E_{MBS} = -1114.89049326 \text{ Ha}$$

$$E_{K+} = -28.095491411 \text{ Ha}$$

Potassium exchange energy

$$\begin{aligned} &= [(-1114.89049326 \text{ Ha} + -28.095491411 \text{ Ha}) \\ &\quad - (-1139.71627736 \text{ Ha} + -3.097986909 \text{ Ha})] \times \frac{2625.5 \frac{\text{kJ}}{\text{mol}}}{\text{Ha}} \\ &= -450.85 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

Binding Site 6 Sample Calculations

$$\text{Potassium} - \text{exchange energy} = E_{\text{products}} - E_{\text{reactants}} = [(E_{\text{MBS}}) - (E_{\text{BS}} + E_{\text{MC}})]$$

Cu(II):

$$\text{Potassium} - \text{exchange energy} = E_{\text{products}} - E_{\text{reactants}} = [(E_{\text{MBS}}) - (E_{\text{BS}} + E_{\text{MC}})]$$

$$E_{\text{BS}} = -1377.66555311 \text{ Ha}$$

$$E_{\text{MC}} = -195.608877521 \text{ Ha}$$

$$E_{\text{MBS}} = -1573.46663249 \text{ Ha}$$

$$E_{\text{K}^+} = -28.095491411 \text{ Ha}$$

Potassium exchange energy

$$= [(-1573.46663249 \text{ Ha})$$

$$- (-1377.66555311 \text{ Ha} + -195.608877521 \text{ Ha})] \times \frac{2625.5 \frac{\text{kJ}}{\text{mol}}}{\text{Ha}}$$

$$= -504.63 \frac{\text{kJ}}{\text{mol}}$$

Pb(II):

$$\text{Potassium} - \text{exchange energy} = E_{\text{products}} - E_{\text{reactants}} = [(E_{\text{MBS}}) - (E_{\text{BS}} + E_{\text{MC}})]$$

$$E_{\text{BS}} = -1377.66555311 \text{ Ha}$$

$$E_{\text{MC}} = -3.097986909 \text{ Ha}$$

$$E_{\text{MBS}} = -1380.84182692 \text{ Ha}$$

$$E_{\text{K}^+} = -28.095491411 \text{ Ha}$$

Potassium exchange energy

$$= [(-1380.84182692 \text{ Ha}) - (-1377.66555311 \text{ Ha} + -3.097986909 \text{ Ha})]$$

$$\times \frac{2625.5 \frac{\text{kJ}}{\text{mol}}}{\text{Ha}} = -205.54 \frac{\text{kJ}}{\text{mol}}$$

Appendix C: Data Tables

Table C.1. Potassium Exchange Energies

Binding Site	Copper Ion Energy (Hartree)	Potassium Ion Energy (Hartree)	Lead Ion Energy (Hartree)	Reactant Binding Site Energy (Hartree)	Copper Product Binding Site Energy (Hartree)	Lead Product Binding Site Energy (Hartree)	Copper Potassium Exchange Energy (kJ/mol)	Lead Potassium Exchange Energy (kJ/mol)	Binding Site
4A	-195.6088775	-28.09549141	-3.097986909	-986.8361015	-1154.598261	-961.9828473	-653.15	-378.73	4A
4B	-195.6088775	-28.09549141	-3.097986909	-986.8331641	-1154.588482	-961.9800448	-635.19	-379.08	4B
4C	-195.6088775	-28.09549141	-3.097986909	-986.8302629	-1154.584317	-961.9587339	-631.87	-330.75	4C
8A	-195.6088775	-28.09549141	-3.097986909	-449.5982722	-617.3518075	-424.7425169	-630.51	-372.16	8A
8B	-195.6088775	-28.09549141	-3.097986909	-449.5983917	-617.3495762	-424.7419516	-624.34	-370.36	8B
7	-195.6088775	-28.09549141	-3.097986909	-374.3742102	-542.1208786	-349.5047695	-612.48	-336.23	7
3B	-195.6088775	-28.09549141	-3.097986909	-676.237004	-843.9836563	-651.3665203	-612.44	-333.49	3B
1A	-195.6088775	-28.09549141	-3.097986909	-523.6280423	-691.362052	-498.7622114	-579.25	-345.71	1A
2	-195.6088775	-28.09549141	-3.097986909	-903.7936924	-1071.513403	-878.9042899	-541.70	-283.82	2
1B	-195.6088775	-28.09549141	-3.097986909	-523.6558894	-691.3589788	-498.7591543	-498.07	-264.57	1B
3A	-195.6088775	-28.09549141	-3.097986909	-676.2496591	-843.952643	-651.359975	-497.79	-283.08	3A
5	-195.6088775	0	-3.097986909	-614.8057959	-810.5920727	-617.9541074	-465.76	-132.13	5
6	-195.6088775	0	-3.097986909	-1377.665553	-1573.466632	-1380.841827	-504.63	-205.54	6
9	-195.6088775	0	-3.097986909	-498.0956043	-693.8607479	-501.2480219	-410.28	-142.91	9
10	-195.6088775	0	-3.097986909	-382.6218199	-578.3681752	-385.7877863	-360.95	-178.48	10

Table C.2. Potassium Exchange Energies with One Explicit Water Molecule

Binding Site	Copper Ion Energy (Hartree)	Potassium Ion Energy (Hartree)	Lead Ion Energy (Hartree)	Reactant Binding Site Energy (Hartree)	Copper Product Binding Site Energy (Hartree)	Lead Product Binding Site Energy (Hartree)	Copper Potassium Exchange Energy (kJ/mol)	Lead Potassium Exchange Energy (kJ/mol)	Binding Site
1A	-195.6088775	-28.09549141	-3.097986909	-600.0621605	-767.8358155	-575.2200069	-683.34	-407.87	1A
4A	-195.6088775	-28.09549141	-3.097986909	-1063.270452	-1231.069151	-1038.41866	-749.09	-382.57	4A
4C	-195.6088775	-28.09549141	-3.097986909	-1063.264788	-1231.061447	-1038.418465	-743.73	-396.93	4C
4B	-195.6088775	-28.09549141	-3.097986909	-1063.267379	-1231.062663	-1038.435679	-740.12	-435.32	4B
7	-195.6088775	-28.09549141	-3.097986909	-450.8085703	-618.601401	-425.9641561	-733.68	-401.94	7
8A	-195.6088775	-28.09549141	-3.097986909	-526.0326477	-693.8256995	-501.1979353	-734.26	-427.41	8A
8B	-195.6088775	-28.09549141	-3.097986909	-526.0328297	-693.8253487	-501.1819928	-732.86	-385.08	8B
3B	-195.6088775	-28.09549141	-3.097986909	-752.6714387	-920.454627	-727.8269225	-708.37	-401.67	3B
2	-195.6088775	-28.09549141	-3.097986909	-980.2280669	-1147.991314	-955.3689898	-656.01	-363.44	2
3A	-195.6088775	-28.09549141	-3.097986909	-752.6839834	-920.4379657	-727.825494	-631.69	-364.98	3A
1B	-195.6088775	-28.09549141	-3.097986909	-600.090263	-767.8337625	-575.2248111	-604.16	-346.70	1B

Table C.3. Potassium Exchange Energies with Two Explicit Water Molecules

Binding Site	Copper Ion Energy (Hartree)	Potassium Ion Energy (Hartree)	Lead Ion Energy (Hartree)	Reactant Binding Site Energy (Hartree)	Copper Product Binding Site Energy (Hartree)	Lead Product Binding Site Energy (Hartree)	Copper Potassium Exchange Energy (kJ/mol)	Lead Potassium Exchange Energy (kJ/mol)	Binding Site
1A	-195.6088775	-28.09549141	-3.097986909	-676.505605	-844.3003937	-651.6702232	-738.82	-425.65	1A
4A	-195.6088775	-28.09549141	-3.097986909	-1139.716277	-1307.513918	-1114.890493	-746.31	-450.85	4A
4C	-195.6088775	-28.09549141	-3.097986909	-1139.711251	-1307.506856	-1114.872052	-740.97	-415.63	4C
4B	-195.6088775	-28.09549141	-3.097986909	-1139.714635	-1307.513775	-1114.888351	-750.25	-449.54	4B
7	-195.6088775	-28.09549141	-3.097986909	-527.2559019	-695.0498314	-502.4188501	-736.57	-421.27	7
8A	-195.6088775	-28.09549141	-3.097986909	-602.478688	-770.270553	-577.6470581	-731.15	-435.50	8A
8B	-195.6088775	-28.09549141	-3.097986909	-602.4785304	-770.2719016	-577.636851	-735.10	-409.12	8B
3B	-195.6088775	-28.09549141	-3.097986909	-829.1052447	-996.8841908	-804.2546088	-697.23	-385.60	3B
2	-195.6088775	-28.09549141	-3.097986909	-1056.668382	-1224.450734	-1031.801215	-706.17	-342.20	2
3A	-195.6088775	-28.09549141	-3.097986909	-829.1262389	-996.8699543	-804.2595516	-604.73	-343.46	3A
1B	-195.6088775	-28.09549141	-3.097986909	-676.5196201	-844.2728075	-651.6568407	-629.60	-353.72	1B

Table C.4. Cation Energies and Radii

Cation	Cation Energy	Effective Ionic
Cu(2+)	-195.6088775	0.73
Pb(2+)	-3.097986909	1.19
Cd(2+)	-47.82991788	0.95
Ni(2+)	-168.8386999	0.69
Cr(3+)	-85.50265371	0.615
Hg(2+)	-42.51614184	1.02
Zn(2+)	-65.3143933	0.74
As(3+)	-4.954371372	0.58
Na(1+)	-0.1592124	1.02
Ca(2+)	-36.44064254	1.00
Au(3+)	-134.3135243	0.85
Bi(3+)	-4.596814359	1.03
Ba(2+)	-25.16802294	1.35
Be(2+)	-14.34497588	0.45
Ti(4+)	-56.84740553	0.605
Mg(2+)	-0.628838914	0.72
Ga(3+)	-0.975216817	0.62
Tl(3+)	-50.62566709	0.885
Al(3+)	-0.950072307	0.535
V(3+)	-70.55655274	0.64
Ag(1+)	-145.6303413	1.15
Pd(2+)	-126.2463587	0.86
Pt(2+)	-118.6900327	0.80
Fe(2+)	-122.9495671	0.61
Mo(3+)	-66.81833004	0.69
Sb(3+)	-4.451881831	0.76

Table C.5. Cation Potassium Exchange Energies for Linear Fitting

Binding Site	4A	4B	4C	3B
Potassium Ion Energy (Hartree)	-28.09549141	-28.09549141	-28.09549141	-28.09549141
Reactant Binding Site Energy (Hartree)	-986.8361015	-986.8331641	-986.8302629	-676.237004
Cu Product Binding Site Energy (Hartree)	-1154.598261	-1154.588482	-1154.584317	-843.9836563
Pb Product Binding Site Energy (Hartree)	-961.9828473	-961.9800448	-961.9587339	-651.3665203
Cd Product Binding Site Energy (Hartree)	-1006.599963	-1006.599163	-1006.594266	-695.9997298
Ni Product Binding Site Energy (Hartree)	-1127.739196	-1127.736651	-1127.707552	-817.1278006
Cr Product Binding Site Energy (Hartree)	-1044.603739	-1044.591628	-1044.586666	-
Hg Product Binding Site Energy (Hartree)	-1001.271937	-1001.26521	-1001.267885	-690.6739844
Zn Product Binding Site Energy (Hartree)	-1024.117846	-1024.11668	-1024.104686	-713.5116034
As Product Binding Site Energy (Hartree)	-964.2821391	-964.2674939	-964.2725861	-653.6188916
Na Product Binding Site Energy (Hartree)	-958.9040598	-958.9021333	-958.8985502	-648.3036428
Ca Product Binding Site Energy (Hartree)	-995.2027641	-995.2036615	-995.1951594	-684.6014389
Au Product Binding Site Energy (Hartree)	-1093.628086	-1093.607289	-1093.617641	-782.9760095
Bi Product Binding Site Energy (Hartree)	-963.6833219	-963.6743241	-963.637453	-653.0436587
Ba Product Binding Site Energy (Hartree)	-983.9095729	-983.907013	-983.9039821	-
Be Product Binding Site Energy (Hartree)	-973.2658748	-973.2635939	-973.2268206	-662.6330338
Ti Product Binding Site Energy (Hartree)	-1016.196878	-1016.188677	-1016.175048	-705.5849558
Mg Product Binding Site Energy (Hartree)	-959.430699	-959.4302244	-959.4141946	-648.8206595
Ga Product Binding Site Energy (Hartree)	-960.2809126	-960.2594496	-960.2660031	-649.6262989
Tl Product Binding Site Energy (Hartree)	-1009.89291	-1009.870925	-1009.87881	-699.2377345
Al Product Binding Site Energy (Hartree)	-960.2040367	-960.1887345	-960.190085	-649.5754732
V Product Binding Site Energy (Hartree)	-1029.586469	-1029.598066	-1029.590883	-718.9765969
Ag Product Binding Site Energy (Hartree)	-1104.39495	-1104.392306	-1104.390196	-793.7955953
Pd Product Binding Site Energy (Hartree)	-1085.16579	-1085.150995	-1085.16189	-774.548277
Pt Product Binding Site Energy (Hartree)	-1077.561145	-1077.557846	-1077.552886	-766.9494724
Fe Product Binding Site Energy (Hartree)	-1081.85415	-1081.850572	-1081.801344	-771.2467776
Mo Product Binding Site Energy (Hartree)	-1025.789299	-1025.798926	-1025.791584	-715.1940591
Sb Product Binding Site Energy (Hartree)	-963.6112676	-963.6002975	-963.5640237	-652.9632207
Cu Potassium Exchange Energy (kJ/mol)	-653.15	-635.19	-631.87	-612.44
Pb Potassium Exchange Energy (kJ/mol)	-378.73	-379.08	-330.75	-333.49
Cd Potassium Exchange Energy (kJ/mol)	-77.28	-82.89	-77.65	-74.30
Ni Potassium Exchange Energy (kJ/mol)	-419.78	-420.81	-352.03	-387.49
Cr Potassium Exchange Energy (kJ/mol)	-946.43	-922.34	-916.93	-
Hg Potassium Exchange Energy (kJ/mol)	-39.87	-29.92	-44.56	-42.87
Zn Potassium Exchange Energy (kJ/mol)	-164.99	-169.64	-145.77	-146.23
As Potassium Exchange Energy (kJ/mol)	-1541.58	-1510.84	-1531.83	-1373.16
Na Potassium Exchange Energy (kJ/mol)	-11.13	-13.78	-11.99	-7.66
Ca Potassium Exchange Energy (kJ/mol)	-56.48	-66.55	-51.84	-50.63
Au Potassium Exchange Energy (kJ/mol)	-1506.91	-1460.02	-1494.81	-1367.81
Bi Potassium Exchange Energy (kJ/mol)	-908.15	-892.24	-803.05	-801.65
Ba Potassium Exchange Energy (kJ/mol)	-2.47	-3.46	-3.12	-
Be Potassium Exchange Energy (kJ/mol)	-473.35	-475.07	-386.14	-384.75
Ti Potassium Exchange Energy (kJ/mol)	-1598.57	-1584.75	-1556.58	-1564.90
Mg Potassium Exchange Energy (kJ/mol)	-160.81	-167.28	-132.81	-132.08
Ga Potassium Exchange Energy (kJ/mol)	-1483.63	-1434.99	-1459.82	-1337.87
Tl Potassium Exchange Energy (kJ/mol)	-1382.67	-1332.67	-1360.99	-1235.44
Al Potassium Exchange Energy (kJ/mol)	-1347.81	-1315.35	-1326.51	-1270.45
V Potassium Exchange Energy (kJ/mol)	-759.57	-797.73	-786.49	-731.28
Ag Potassium Exchange Energy (kJ/mol)	-63.01	-63.78	-65.86	-62.33
Pd Potassium Exchange Energy (kJ/mol)	-469.50	-438.36	-474.58	-421.15
Pt Potassium Exchange Energy (kJ/mol)	-342.63	-341.68	-336.28	-309.62
Fe Potassium Exchange Energy (kJ/mol)	-430.51	-428.83	-307.20	-408.78
Mo Potassium Exchange Energy (kJ/mol)	-604.81	-637.80	-626.14	-614.94
Sb Potassium Exchange Energy (kJ/mol)	-1099.50	-1078.41	-990.79	-970.98

Table C.6. Physical Property Constants

Constant	Value	Units	Note
π	3.141592654		
ϵ_0	8.85419×10^{-12}	F/m	Vacuum permittivity
ϵ	80.2		Dielectric permittivity of water at 20 degrees Celsius (Archer and Wang, 1990)
Elementary charge	1.60218×10^{-19}	C	
Avogadro's number	6.02214×10^{23}	mol^{-1}	

Table C.7. Alkali and Alkaline Earth Metals Data

Binding Site and Metal	Cation Formal Charge	Anion Formal Charge	Cation Radius (m)	Cation Surface Area (m ²)	Cation Formal Surface Charge Density (C/m ²)	Anion Radius (m)	Coulombic Radius (m)	Electric Potential Energy (J)	Cation Formal Born Energy (J)	Potassium Exchange Energy (kJ/mol)
4A Sodium	1	2	1.02E-10	1.31E-19	1.23	1.4E-10	2.42E-10	-2.38E-20	1.41E-20	-11.13
4B Sodium	1	2	1.02E-10	1.31E-19	1.23	1.4E-10	2.42E-10	-2.38E-20	1.41E-20	-13.78
4C Sodium	1	2	1.02E-10	1.31E-19	1.23	1.4E-10	2.42E-10	-2.38E-20	1.41E-20	-11.99
3B Sodium	1	2	1.02E-10	1.31E-19	1.23	1.4E-10	2.42E-10	-2.38E-20	1.41E-20	-7.66
4A Calcium	2	2	1E-10	1.26E-19	2.55	1.4E-10	2.40E-10	-4.79E-20	5.75E-20	-56.48
4B Calcium	2	2	1E-10	1.26E-19	2.55	1.4E-10	2.40E-10	-4.79E-20	5.75E-20	-66.55
4C Calcium	2	2	1E-10	1.26E-19	2.55	1.4E-10	2.40E-10	-4.79E-20	5.75E-20	-51.84
3B Calcium	2	2	1E-10	1.26E-19	2.55	1.4E-10	2.40E-10	-4.79E-20	5.75E-20	-50.63
4A Beryllium	2	2	4.5E-11	2.54E-20	12.59	1.4E-10	1.85E-10	-6.22E-20	1.28E-19	-473.35
4B Beryllium	2	2	4.5E-11	2.54E-20	12.59	1.4E-10	1.85E-10	-6.22E-20	1.28E-19	-475.07
4C Beryllium	2	2	4.5E-11	2.54E-20	12.59	1.4E-10	1.85E-10	-6.22E-20	1.28E-19	-386.14
3B Beryllium	2	2	4.5E-11	2.54E-20	12.59	1.4E-10	1.85E-10	-6.22E-20	1.28E-19	-384.75
4A Barium	1	2	1.35E-10	2.29E-19	0.70	1.4E-10	2.75E-10	-2.09E-20	1.07E-20	-2.47
4B Barium	1	2	1.35E-10	2.29E-19	0.70	1.4E-10	2.75E-10	-2.09E-20	1.07E-20	-3.46
4C Barium	1	2	1.35E-10	2.29E-19	0.70	1.4E-10	2.75E-10	-2.09E-20	1.07E-20	-3.12
4A Magnesium	2	2	7.2E-11	6.51E-20	4.92	1.4E-10	2.12E-10	-5.43E-20	7.99E-20	-160.81
4B Magnesium	2	2	7.2E-11	6.51E-20	4.92	1.4E-10	2.12E-10	-5.43E-20	7.99E-20	-167.28
4C Magnesium	2	2	7.2E-11	6.51E-20	4.92	1.4E-10	2.12E-10	-5.43E-20	7.99E-20	-132.81
3B Magnesium	2	2	7.2E-11	6.51E-20	4.92	1.4E-10	2.12E-10	-5.43E-20	7.99E-20	-132.08

Table C.8. Transition Metals Data

Binding Site and Metal	Cation Formal Charge	Anion Formal Charge	Cation Radius (m)	Cation Surface Area (m ²)	Cation Formal Surface Charge Density (C/m ²)	Anion Radius (m)	Coulombic Radius (m)	Electric Potential Energy (J)	Cation Formal Born Energy (J)	Potassium Exchange Energy (kJ/mol)
4A Copper	2	2	7.3E-11	6.70E-20	4.79	1.4E-10	2.13E-10	-5.40E-20	7.88E-20	-653.15
4B Copper	2	2	7.3E-11	6.70E-20	4.79	1.4E-10	2.13E-10	-5.40E-20	7.88E-20	-635.19
4C Copper	2	2	7.3E-11	6.70E-20	4.79	1.4E-10	2.13E-10	-5.40E-20	7.88E-20	-631.87
3B Copper	2	2	7.3E-11	6.70E-20	4.79	1.4E-10	2.13E-10	-5.40E-20	7.88E-20	-612.44
4A Nickel	2	2	6.9E-11	5.98E-20	5.36	1.4E-10	2.09E-10	-5.51E-20	8.34E-20	-419.78
4B Nickel	2	2	6.9E-11	5.98E-20	5.36	1.4E-10	2.09E-10	-5.51E-20	8.34E-20	-420.81
4C Nickel	2	2	6.9E-11	5.98E-20	5.36	1.4E-10	2.09E-10	-5.51E-20	8.34E-20	-352.03
3B Nickel	2	2	6.9E-11	5.98E-20	5.36	1.4E-10	2.09E-10	-5.51E-20	8.34E-20	-387.49
4A Cadmium	2	2	9.5E-11	1.13E-19	2.83	1.4E-10	2.35E-10	-4.90E-20	6.06E-20	-77.28
4B Cadmium	2	2	9.5E-11	1.13E-19	2.83	1.4E-10	2.35E-10	-4.90E-20	6.06E-20	-82.89
4C Cadmium	2	2	9.5E-11	1.13E-19	2.83	1.4E-10	2.35E-10	-4.90E-20	6.06E-20	-77.65
3B Cadmium	2	2	9.5E-11	1.13E-19	2.83	1.4E-10	2.35E-10	-4.90E-20	6.06E-20	-74.30
4A Chromium	3	2	6.15E-11	4.75E-20	10.11	1.4E-10	2.02E-10	-8.57E-20	2.10E-19	-946.43
4B Chromium	3	2	6.15E-11	4.75E-20	10.11	1.4E-10	2.02E-10	-8.57E-20	2.10E-19	-922.34
4C Chromium	3	2	6.15E-11	4.75E-20	10.11	1.4E-10	2.02E-10	-8.57E-20	2.10E-19	-916.93
4A Zinc	2	2	7.4E-11	6.88E-20	4.66	1.4E-10	2.14E-10	-5.38E-20	7.77E-20	-164.99
4B Zinc	2	2	7.4E-11	6.88E-20	4.66	1.4E-10	2.14E-10	-5.38E-20	7.77E-20	-169.64
4C Zinc	2	2	7.4E-11	6.88E-20	4.66	1.4E-10	2.14E-10	-5.38E-20	7.77E-20	-145.77
3B Zinc	2	2	7.4E-11	6.88E-20	4.66	1.4E-10	2.14E-10	-5.38E-20	7.77E-20	-146.23
4A Gold	3	2	8.5E-11	9.08E-20	5.29	1.4E-10	2.25E-10	-7.67E-20	1.52E-19	-1506.91
4B Gold	3	2	8.5E-11	9.08E-20	5.29	1.4E-10	2.25E-10	-7.67E-20	1.52E-19	-1460.02
4C Gold	3	2	8.5E-11	9.08E-20	5.29	1.4E-10	2.25E-10	-7.67E-20	1.52E-19	-1494.81
3B Gold	3	2	8.5E-11	9.08E-20	5.29	1.4E-10	2.25E-10	-7.67E-20	1.52E-19	-1367.81
4A Titanium	4	2	6.05E-11	4.60E-20	13.93	1.4E-10	2.01E-10	-1.15E-19	3.80E-19	-1598.57
4B Titanium	4	2	6.05E-11	4.60E-20	13.93	1.4E-10	2.01E-10	-1.15E-19	3.80E-19	-1584.75
4C Titanium	4	2	6.05E-11	4.60E-20	13.93	1.4E-10	2.01E-10	-1.15E-19	3.80E-19	-1556.58
3B Titanium	4	2	6.05E-11	4.60E-20	13.93	1.4E-10	2.01E-10	-1.15E-19	3.80E-19	-1564.90
4A Mercury	2	2	1.02E-10	1.31E-19	2.45	1.4E-10	2.42E-10	-4.75E-20	5.64E-20	-39.87
4B Mercury	2	2	1.02E-10	1.31E-19	2.45	1.4E-10	2.42E-10	-4.75E-20	5.64E-20	-29.92
4C Mercury	2	2	1.02E-10	1.31E-19	2.45	1.4E-10	2.42E-10	-4.75E-20	5.64E-20	-44.56
3B Mercury	2	2	1.02E-10	1.31E-19	2.45	1.4E-10	2.42E-10	-4.75E-20	5.64E-20	-42.87
4A Vanadium	3	2	6.4E-11	5.15E-20	9.34	1.4E-10	2.04E-10	-8.46E-20	2.02E-19	-759.57
4B Vanadium	3	2	6.4E-11	5.15E-20	9.34	1.4E-10	2.04E-10	-8.46E-20	2.02E-19	-797.73
4C Vanadium	3	2	6.4E-11	5.15E-20	9.34	1.4E-10	2.04E-10	-8.46E-20	2.02E-19	-786.49
3B Vanadium	3	2	6.4E-11	5.15E-20	9.34	1.4E-10	2.04E-10	-8.46E-20	2.02E-19	-731.28
4A Silver	1	2	1.15E-10	1.66E-19	0.96	1.4E-10	2.55E-10	-2.26E-20	1.25E-20	-63.01
4B Silver	1	2	1.15E-10	1.66E-19	0.96	1.4E-10	2.55E-10	-2.26E-20	1.25E-20	-63.78
4C Silver	1	2	1.15E-10	1.66E-19	0.96	1.4E-10	2.55E-10	-2.26E-20	1.25E-20	-65.86
3B Silver	1	2	1.15E-10	1.66E-19	0.96	1.4E-10	2.55E-10	-2.26E-20	1.25E-20	-62.33
4A Palladium	2	2	8.6E-11	9.29E-20	3.45	1.4E-10	2.26E-10	-5.09E-20	6.69E-20	-469.50
4B Palladium	2	2	8.6E-11	9.29E-20	3.45	1.4E-10	2.26E-10	-5.09E-20	6.69E-20	-438.36
4C Palladium	2	2	8.6E-11	9.29E-20	3.45	1.4E-10	2.26E-10	-5.09E-20	6.69E-20	-474.58
3B Palladium	2	2	8.6E-11	9.29E-20	3.45	1.4E-10	2.26E-10	-5.09E-20	6.69E-20	-421.15
4A Platinum	2	2	8E-11	8.04E-20	3.98	1.4E-10	2.20E-10	-5.23E-20	7.19E-20	-342.63
4B Platinum	2	2	8E-11	8.04E-20	3.98	1.4E-10	2.20E-10	-5.23E-20	7.19E-20	-341.68
4C Platinum	2	2	8E-11	8.04E-20	3.98	1.4E-10	2.20E-10	-5.23E-20	7.19E-20	-336.28
3B Platinum	2	2	8E-11	8.04E-20	3.98	1.4E-10	2.20E-10	-5.23E-20	7.19E-20	-309.62
4A Iron	2	2	6.1E-11	4.68E-20	6.85	1.4E-10	2.01E-10	-5.72E-20	9.43E-20	-430.51
4B Iron	2	2	6.1E-11	4.68E-20	6.85	1.4E-10	2.01E-10	-5.72E-20	9.43E-20	-428.83
4C Iron	2	2	6.1E-11	4.68E-20	6.85	1.4E-10	2.01E-10	-5.72E-20	9.43E-20	-307.20
3B Iron	2	2	6.1E-11	4.68E-20	6.85	1.4E-10	2.01E-10	-5.72E-20	9.43E-20	-408.78
4A Molybdenum	3	2	6.9E-11	5.98E-20	8.03	1.4E-10	2.09E-10	-8.26E-20	1.88E-19	-604.81
4B Molybdenum	3	2	6.9E-11	5.98E-20	8.03	1.4E-10	2.09E-10	-8.26E-20	1.88E-19	-637.80
4C Molybdenum	3	2	6.9E-11	5.98E-20	8.03	1.4E-10	2.09E-10	-8.26E-20	1.88E-19	-626.14
3B Molybdenum	3	2	6.9E-11	5.98E-20	8.03	1.4E-10	2.09E-10	-8.26E-20	1.88E-19	-614.94

Table C.9. Post-Transition Metals and Metalloids Data

Binding Site and Metal	Cation Formal Charge	Anion Formal Charge	Cation Radius (m)	Cation Surface Area (m ²)	Cation Formal Surface Charge Density (C/m ²)	Anion Radius (m)	Coulombic Radius (m)	Electric Potential Energy (J)	Cation Formal Born Energy (J)	Potassium Exchange Energy (kJ/mol)
4A Lead	2	2	1.19E-10	1.78E-19	1.80	1.4E-10	2.59E-10	-4.44E-20	4.83E-20	-378.73
4B Lead	2	2	1.19E-10	1.78E-19	1.80	1.4E-10	2.59E-10	-4.44E-20	4.83E-20	-379.08
4C Lead	2	2	1.19E-10	1.78E-19	1.80	1.4E-10	2.59E-10	-4.44E-20	4.83E-20	-330.75
3B Lead	2	2	1.19E-10	1.78E-19	1.80	1.4E-10	2.59E-10	-4.44E-20	4.83E-20	-333.49
4A Bismuth	3	2	1.03E-10	1.33E-19	3.61	1.4E-10	2.43E-10	-7.10E-20	1.26E-19	-908.15
4B Bismuth	3	2	1.03E-10	1.33E-19	3.61	1.4E-10	2.43E-10	-7.10E-20	1.26E-19	-892.24
4C Bismuth	3	2	1.03E-10	1.33E-19	3.61	1.4E-10	2.43E-10	-7.10E-20	1.26E-19	-803.05
3B Bismuth	3	2	1.03E-10	1.33E-19	3.61	1.4E-10	2.43E-10	-7.10E-20	1.26E-19	-801.65
4A Arsenic	3	2	5.8E-11	4.23E-20	11.37	1.4E-10	1.98E-10	-8.72E-20	2.23E-19	-1541.58
4B Arsenic	3	2	5.8E-11	4.23E-20	11.37	1.4E-10	1.98E-10	-8.72E-20	2.23E-19	-1510.84
4C Arsenic	3	2	5.8E-11	4.23E-20	11.37	1.4E-10	1.98E-10	-8.72E-20	2.23E-19	-1531.83
3B Arsenic	3	2	5.8E-11	4.23E-20	11.37	1.4E-10	1.98E-10	-8.72E-20	2.23E-19	-1373.16
4A Gallium	3	2	6.2E-11	4.83E-20	9.95	1.4E-10	2.02E-10	-8.54E-20	2.09E-19	-1483.63
4B Gallium	3	2	6.2E-11	4.83E-20	9.95	1.4E-10	2.02E-10	-8.54E-20	2.09E-19	-1434.99
4C Gallium	3	2	6.2E-11	4.83E-20	9.95	1.4E-10	2.02E-10	-8.54E-20	2.09E-19	-1459.82
3B Gallium	3	2	6.2E-11	4.83E-20	9.95	1.4E-10	2.02E-10	-8.54E-20	2.09E-19	-1337.87
4A Thallium	3	2	8.85E-11	9.84E-20	4.88	1.4E-10	2.29E-10	-7.55E-20	1.46E-19	-1382.67
4B Thallium	3	2	8.85E-11	9.84E-20	4.88	1.4E-10	2.29E-10	-7.55E-20	1.46E-19	-1332.67
4C Thallium	3	2	8.85E-11	9.84E-20	4.88	1.4E-10	2.29E-10	-7.55E-20	1.46E-19	-1360.99
3B Thallium	3	2	8.85E-11	9.84E-20	4.88	1.4E-10	2.29E-10	-7.55E-20	1.46E-19	-1235.44
4A Aluminum	3	2	5.35E-11	3.60E-20	13.36	1.4E-10	1.94E-10	-8.92E-20	2.42E-19	-1347.81
4B Aluminum	3	2	5.35E-11	3.60E-20	13.36	1.4E-10	1.94E-10	-8.92E-20	2.42E-19	-1315.35
4C Aluminum	3	2	5.35E-11	3.60E-20	13.36	1.4E-10	1.94E-10	-8.92E-20	2.42E-19	-1326.51
3B Aluminum	3	2	5.35E-11	3.60E-20	13.36	1.4E-10	1.94E-10	-8.92E-20	2.42E-19	-1270.45
4A Antimony	3	2	7.60E-11	7.26E-20	6.62	1.4E-10	2.16E-10	-7.99E-20	1.70E-19	-1099.50
4B Antimony	3	2	7.60E-11	7.26E-20	6.62	1.4E-10	2.16E-10	-7.99E-20	1.70E-19	-1078.41
4C Antimony	3	2	7.60E-11	7.26E-20	6.62	1.4E-10	2.16E-10	-7.99E-20	1.70E-19	-990.79
3B Antimony	3	2	7.60E-11	7.26E-20	6.62	1.4E-10	2.16E-10	-7.99E-20	1.70E-19	-970.98

Table C.10. Alkali and Alkaline Earth Metals Physical Properties

Binding Site and Metal	Born Self-Energy (kJ/mol)	Electric Potential Energy (kJ/mol)	ln(-Potassium Exchange Energy)	ln(Formal Surface Charge Density)	ln(-Electric Potential Energy)	ln(Born Self- Energy)
4A Sodium	8.49	-14.32	2.41	0.20	2.66	2.14
4B Sodium	8.49	-14.32	2.62	0.20	2.66	2.14
4C Sodium	8.49	-14.32	2.48	0.20	2.66	2.14
3B Sodium	8.49	-14.32	2.04	0.20	2.66	2.14
4A Calcium	34.65	-28.87	4.03	0.94	3.36	3.55
4B Calcium	34.65	-28.87	4.20	0.94	3.36	3.55
4C Calcium	34.65	-28.87	3.95	0.94	3.36	3.55
3B Calcium	34.65	-28.87	3.92	0.94	3.36	3.55
4A Beryllium	76.99	-37.46	6.16	2.53	3.62	4.34
4B Beryllium	76.99	-37.46	6.16	2.53	3.62	4.34
4C Beryllium	76.99	-37.46	5.96	2.53	3.62	4.34
3B Beryllium	76.99	-37.46	5.95	2.53	3.62	4.34
4A Barium	6.42	-12.60	0.90	-0.36	2.53	1.86
4B Barium	6.42	-12.60	1.24	-0.36	2.53	1.86
4C Barium	6.42	-12.60	1.14	-0.36	2.53	1.86
4A Magnesium	48.12	-32.69	5.08	1.59	3.49	3.87
4B Magnesium	48.12	-32.69	5.12	1.59	3.49	3.87
4C Magnesium	48.12	-32.69	4.89	1.59	3.49	3.87
3B Magnesium	48.12	-32.69	4.88	1.59	3.49	3.87

Table C.11. Transition Metals Physical Properties

Binding Site and Metal	Born Self-Energy (kJ/mol)	Electric Potential Energy (kJ/mol)	ln(-Potassium Exchange Energy)	ln(Formal Surface Charge Density)	ln(-Electric Potential Energy)	ln(Born Self- Energy)
4A Copper	47.46	-32.53	6.48	1.57	3.48	3.86
4B Copper	47.46	-32.53	6.45	1.57	3.48	3.86
4C Copper	47.46	-32.53	6.45	1.57	3.48	3.86
3B Copper	47.46	-32.53	6.42	1.57	3.48	3.86
4A Nickel	50.21	-33.16	6.04	1.68	3.50	3.92
4B Nickel	50.21	-33.16	6.04	1.68	3.50	3.92
4C Nickel	50.21	-33.16	5.86	1.68	3.50	3.92
3B Nickel	50.21	-33.16	5.96	1.68	3.50	3.92
4A Cadmium	36.47	-29.49	4.35	1.04	3.38	3.60
4B Cadmium	36.47	-29.49	4.42	1.04	3.38	3.60
4C Cadmium	36.47	-29.49	4.35	1.04	3.38	3.60
3B Cadmium	36.47	-29.49	4.31	1.04	3.38	3.60
4A Chromium	126.76	-51.58	6.85	2.31	3.94	4.84
4B Chromium	126.76	-51.58	6.83	2.31	3.94	4.84
4C Chromium	126.76	-51.58	6.82	2.31	3.94	4.84
4A Zinc	46.82	-32.38	5.11	1.54	3.48	3.85
4B Zinc	46.82	-32.38	5.13	1.54	3.48	3.85
4C Zinc	46.82	-32.38	4.98	1.54	3.48	3.85
3B Zinc	46.82	-32.38	4.99	1.54	3.48	3.85
4A Gold	91.71	-46.20	7.32	1.67	3.83	4.52
4B Gold	91.71	-46.20	7.29	1.67	3.83	4.52
4C Gold	91.71	-46.20	7.31	1.67	3.83	4.52
3B Gold	91.71	-46.20	7.22	1.67	3.83	4.52
4A Titanium	229.07	-69.12	7.38	2.63	4.24	5.43
4B Titanium	229.07	-69.12	7.37	2.63	4.24	5.43
4C Titanium	229.07	-69.12	7.35	2.63	4.24	5.43
3B Titanium	229.07	-69.12	7.36	2.63	4.24	5.43
4A Mercury	33.97	-28.63	3.69	0.90	3.35	3.53
4B Mercury	33.97	-28.63	3.40	0.90	3.35	3.53
4C Mercury	33.97	-28.63	3.80	0.90	3.35	3.53
3B Mercury	33.97	-28.63	3.76	0.90	3.35	3.53
4A Vanadium	121.81	-50.95	6.63	2.23	3.93	4.80
4B Vanadium	121.81	-50.95	6.68	2.23	3.93	4.80
4C Vanadium	121.81	-50.95	6.67	2.23	3.93	4.80
3B Vanadium	121.81	-50.95	6.59	2.23	3.93	4.80
4A Silver	7.53	-13.59	4.14	-0.04	2.61	2.02
4B Silver	7.53	-13.59	4.16	-0.04	2.61	2.02
4C Silver	7.53	-13.59	4.19	-0.04	2.61	2.02
3B Silver	7.53	-13.59	4.13	-0.04	2.61	2.02
4A Palladium	40.29	-30.66	6.15	1.24	3.42	3.70
4B Palladium	40.29	-30.66	6.08	1.24	3.42	3.70
4C Palladium	40.29	-30.66	6.16	1.24	3.42	3.70
3B Palladium	40.29	-30.66	6.04	1.24	3.42	3.70
4A Platinum	43.31	-31.50	5.84	1.38	3.45	3.77
4B Platinum	43.31	-31.50	5.83	1.38	3.45	3.77
4C Platinum	43.31	-31.50	5.82	1.38	3.45	3.77
3B Platinum	43.31	-31.50	5.74	1.38	3.45	3.77
4A Iron	56.80	-34.47	6.06	1.92	3.54	4.04
4B Iron	56.80	-34.47	6.06	1.92	3.54	4.04
4C Iron	56.80	-34.47	5.73	1.92	3.54	4.04
3B Iron	56.80	-34.47	6.01	1.92	3.54	4.04
4A Molybdenum	112.98	-49.73	6.40	2.08	3.91	4.73
4B Molybdenum	112.98	-49.73	6.46	2.08	3.91	4.73
4C Molybdenum	112.98	-49.73	6.44	2.08	3.91	4.73
3B Molybdenum	112.98	-49.73	6.42	2.08	3.91	4.73

Table C.12. Post-Transition Metals and Metalloids Physical Properties

Binding Site and Metal	Born Self-Energy (kJ/mol)	Electric Potential Energy (kJ/mol)	ln(-Potassium Exchange Energy)	ln(Formal Surface Charge Density)	ln(-Electric Potential Energy)	ln(Born Self- Energy)
4A Lead	29.12	-26.75	5.94	0.59	3.29	3.37
4B Lead	29.12	-26.75	5.94	0.59	3.29	3.37
4C Lead	29.12	-26.75	5.80	0.59	3.29	3.37
3B Lead	29.12	-26.75	5.81	0.59	3.29	3.37
4A Bismuth	75.69	-42.77	6.81	1.28	3.76	4.33
4B Bismuth	75.69	-42.77	6.79	1.28	3.76	4.33
4C Bismuth	75.69	-42.77	6.69	1.28	3.76	4.33
3B Bismuth	75.69	-42.77	6.69	1.28	3.76	4.33
4A Arsenic	134.41	-52.50	7.34	2.43	3.96	4.90
4B Arsenic	134.41	-52.50	7.32	2.43	3.96	4.90
4C Arsenic	134.41	-52.50	7.33	2.43	3.96	4.90
3B Arsenic	134.41	-52.50	7.22	2.43	3.96	4.90
4A Gallium	125.74	-51.46	7.30	2.30	3.94	4.83
4B Gallium	125.74	-51.46	7.27	2.30	3.94	4.83
4C Gallium	125.74	-51.46	7.29	2.30	3.94	4.83
3B Gallium	125.74	-51.46	7.20	2.30	3.94	4.83
4A Thallium	88.09	-45.49	7.23	1.59	3.82	4.48
4B Thallium	88.09	-45.49	7.19	1.59	3.82	4.48
4C Thallium	88.09	-45.49	7.22	1.59	3.82	4.48
3B Thallium	88.09	-45.49	7.12	1.59	3.82	4.48
4A Aluminum	145.71	-53.72	7.21	2.59	3.98	4.98
4B Aluminum	145.71	-53.72	7.18	2.59	3.98	4.98
4C Aluminum	145.71	-53.72	7.19	2.59	3.98	4.98
3B Aluminum	145.71	-53.72	7.15	2.59	3.98	4.98
4A Antimony	102.57	-48.12	7.00	1.89	3.87	4.63
4B Antimony	102.57	-48.12	6.98	1.89	3.87	4.63
4C Antimony	102.57	-48.12	6.90	1.89	3.87	4.63
3B Antimony	102.57	-48.12	6.88	1.89	3.87	4.63

Appendix D: Sample Input Files

Binding Site 4A Input Files

Cu(II)

input.xyz

```
Cu 0.00000000 0.00000000 0.00000000
```

input.com

```
#N B3LYP/LANL2DZ OPT SCRF=(PCM,Solvent=Water) UHF Geom=Connectivity
```

```
Copper Ion (2+)
```

```
2 2
```

```
Cu
```

```
1
```

Pb(II)

input.xyz

```
Pb 0.00000000 0.00000000 0.00000000
```

input.com

```
#N B3LYP/LANL2DZ OPT SCRF=(PCM,Solvent=Water) UHF Geom=Connectivity
```

```
Lead Ion (+2)
```

```
2 1
```

```
Pb
```

```
1
```

Reactant Binding Site

input.xyz

```
C 0.00000000 0.00000000 0.00000000
C -1.48044000 -0.40422700 -0.07338300
C -1.86191700 -1.50379500 -0.89236700
C -3.19468800 -1.94853000 -0.99895800
C -4.19698900 -1.26589600 -0.26449800
C -3.88707500 -0.16760200 0.56917700
C -2.50606400 0.22598900 0.64118600
```

```

O   -2.28466900   1.31205800   1.50967900
H   -3.20977600   1.51310600   1.84034400
O   -4.76116900   0.54773200   1.31207400
K   -6.80967100   1.57518000   2.39562400
H   -5.23220300  -1.59538400  -0.33693500
H   -3.55347900  -3.13636300  -1.87975300
O   -0.81098400  -2.15879100  -1.60081800
H   -1.16512200  -2.78250400  -2.26625300
C    0.70373500  -0.58358500   1.23440000
C    1.86586300  -1.36911300   1.06569300
C    2.53818800  -1.92444600   2.17385500
C    2.05499700  -1.69782900   3.47721500
C    0.89737300  -0.91173300   3.65797500
C    0.22936200  -0.35921300   2.54908500
H   -0.65779400   0.25027000   2.69307300
H    0.51784900  -0.72949300   4.66126000
H    2.56894400  -2.12474900   4.33534100
H    3.42921600  -2.52893700   2.01959300
H    2.24709400  -1.55007100   0.06235400
C    0.23917000   1.50991800  -0.21404900
C   -0.41535800   2.16348200  -1.28569500
C   -0.16520600   3.51599300  -1.57660700
C    0.75581900   4.25095000  -0.80016300
C    1.41921600   3.61042000   0.26319900
C    1.16499800   2.25269200   0.54927600
H    1.68918600   1.77858500   1.37389600
H    2.13489200   4.16251000   0.86870900
H    0.95181400   5.29730200  -1.02224300
H   -0.68280800   3.99552100  -2.40469100
H   -1.12962500   1.60835800  -1.89031700
H    0.46635700  -0.48849800  -0.86429500

```

input.com

```

%NProcShared=2
#N B3LYP/LANL2DZ OPT SCRF=(PCM,Solvent=Water) UHF Geom=Connectivity

```

11/27 Binding Site 4a

```

O 1
C
C 1 B1
C 2 B2 1 A1
C 3 B3 2 A2 1 D1
C 4 B4 3 A3 2 D2
C 5 B5 4 A4 3 D3
C 2 B6 3 A5 4 D4
O 7 B7 2 A6 3 D5
H 8 B8 7 A7 2 D6
O 6 B9 7 A8 2 D7
K 10 B10 6 A9 7 D8
H 5 B11 6 A10 7 D9
H 4 B12 3 A11 2 D10
O 3 B13 4 A12 5 D11
H 14 B14 3 A13 4 D12
C 1 B15 2 A14 3 D13

```

C 16 B16 1 A15 2 D14
C 17 B17 16 A16 1 D15
C 18 B18 17 A17 16 D16
C 19 B19 18 A18 17 D17
C 20 B20 19 A19 18 D18
H 21 B21 20 A20 19 D19
H 20 B22 19 A21 18 D20
H 19 B23 18 A22 17 D21
H 18 B24 17 A23 16 D22
H 17 B25 16 A24 1 D23
C 1 B26 2 A25 3 D24
C 27 B27 1 A26 2 D25
C 28 B28 27 A27 1 D26
C 29 B29 28 A28 27 D27
C 30 B30 29 A29 28 D28
C 31 B31 30 A30 29 D29
H 32 B32 31 A31 30 D30
H 31 B33 30 A32 29 D31
H 30 B34 29 A33 28 D32
H 29 B35 28 A34 27 D33
H 28 B36 27 A35 1 D34
H 1 B37 2 A36 3 D35

B1 1.536387687
B2 1.423133613
B3 1.409052660
B4 1.417754550
B5 1.413262326
B6 1.399887728
B7 1.408134124
B8 1.002787416
B9 1.351901995
B10 2.534973459
B11 1.088796348
B12 1.521669494
B13 1.426668409
B14 0.978384060
B15 1.536085207
B16 1.412819089
B17 1.410120089
B18 1.408394865
B19 1.410926796
B20 1.407534752
B21 1.085931784
B22 1.088039832
B23 1.087558016
B24 1.087721026
B25 1.088472334
B26 1.543655282
B27 1.415619283
B28 1.405877598
B29 1.411139301
B30 1.407520161
B31 1.410635376
B32 1.086070279
B33 1.087951224
B34 1.087467735

B35 1.087925569
B36 1.088075257
B37 1.096870546
A1 119.2789986
A2 122.7477644
A3 118.5242830
A4 121.6509629
A5 116.4359547
A6 123.1519151
A7 102.2961237
A8 116.6575814
A9 166.3696599
A10 118.8760916
A11 120.8767012
A12 120.9495752
A13 111.3328471
A14 112.3261263
A15 119.4799152
A16 121.1518025
A17 120.0207158
A18 119.3204720
A19 120.4752742
A20 120.2371052
A21 119.8443599
A22 120.3248991
A23 119.8663007
A24 119.3802529
A25 113.5796997
A26 119.0074857
A27 121.2338263
A28 120.2207532
A29 119.0974089
A30 120.4164816
A31 119.1541757
A32 119.9726462
A33 120.4244126
A34 119.7944096
A35 119.2506815
A36 104.7663499
D1 179.0869781
D2 0.360547980
D3 -0.443630007
D4 0.279883638
D5 178.9210998
D6 179.7155427
D7 -179.4774092
D8 170.6255172
D9 179.5638527
D10 -179.5249559
D11 179.5305293
D12 11.75102385
D13 -97.54452730
D14 124.2898186
D15 -179.8618641
D16 -0.123106920
D17 -0.057515940
D18 0.053549944

D19 -179.6243549
D20 -179.8728339
D21 179.9247919
D22 179.7856169
D23 0.009822646
D24 130.7518659
D25 -46.25765852
D26 -175.8411631
D27 0.236695784
D28 0.147031746
D29 -0.080824843
D30 179.9341806
D31 179.7732059
D32 -179.9984066
D33 -179.8854033
D34 4.543772946
D35 16.61175876

1 2 1 16 1 27 1 38 1
2 3 1 7 2 1 1
3 4 2 2 1 14 1
4 3 2 5 1 13 1
5 6 2 4 1 12 1
6 7 1 5 2 10 1
7 2 2 6 1 8 1
8 7 1 9 1
9 8 1
10 6 1 11 1
11 10 1
12 5 1
13 4 1
14 3 1 15 1
15 14 1
16 1 1 17 1 21 2
17 16 1 18 2 26 1
18 17 2 19 1 25 1
19 18 1 20 2 24 1
20 19 2 21 1 23 1
21 20 1 16 2 22 1
22 21 1
23 20 1
24 19 1
25 18 1
26 17 1
27 1 1 28 2 32 1
28 27 2 29 1 37 1
29 28 1 30 2 36 1
30 29 2 31 1 35 1
31 30 1 32 2 34 1
32 31 2 27 1 33 1
33 32 1
34 31 1
35 30 1
36 29 1
37 28 1
38 1 1

Cu(II) Product Binding Site

input.xyz

```

C      0.00000000  0.00000000  0.00000000
C     -1.12191500 -1.02305600 -0.21741700
C     -0.82145500 -2.25772400 -0.84759900
C     -1.79892400 -3.24822900 -1.06000300
C     -3.12298500 -3.04173900 -0.63667200
C     -3.46296100 -1.83639200 -0.00498000
C     -2.45745400 -0.86187000  0.18342800
O     -2.95556000  0.30067700  0.85035800
H     -2.32871100  1.06789500  0.87728000
O     -4.73943000 -1.55796800  0.45349600
Cu    -5.20347800  0.20805800  1.39521500
H     -3.88481400 -3.79926400 -0.78797100
H     -1.53036100 -4.18056000 -1.55061000
O      0.51111300 -2.43895000 -1.24424700
H      0.65293600 -3.29634700 -1.69570200
C      0.78873100 -0.24725500  1.29686500
C      2.15737300  0.10514700  1.33311900
C      2.92069900 -0.07863200  2.50028700
C      2.32372000 -0.62111800  3.65715300
C      0.96185800 -0.97797800  3.63030700
C      0.20122700 -0.79229300  2.45813600
H     -0.84523100 -1.08505700  2.45633000
H      0.49257800 -1.40074800  4.51534800
H      2.91135600 -0.76718200  4.56002600
H      3.97324900  0.19380500  2.50724500
H      2.62745600  0.52067900  0.44372300
C     -0.47096600  1.46244300 -0.16485600
C     -0.80731500  1.92245900 -1.46172500
C     -1.23103300  3.24551200 -1.67024000
C     -1.32793000  4.14026500 -0.58243000
C     -0.99333500  3.69748400  0.70953200
C     -0.56597400  2.36710000  0.91819400
H     -0.28255100  2.04991700  1.91807300
H     -1.05692400  4.37832900  1.55423900
H     -1.65364300  5.16433800 -0.74392200
H     -1.48072700  3.58127800 -2.67342800
H     -0.73133000  1.24129600 -2.30667400
H      0.70500700 -0.17813200 -0.81976400

```

input.com

```

%NProcShared=2
#N B3LYP/LANL2DZ OPT SCRF=(PCM,Solvent=Water) UHF Geom=Connectivity

11/27 Binding Site 4a Copper Adsorbed

1 2
C
C 1 B1

```

C 2 B2 1 A1
C 3 B3 2 A2 1 D1
C 4 B4 3 A3 2 D2
C 5 B5 4 A4 3 D3
C 2 B6 3 A5 4 D4
O 7 B7 2 A6 3 D5
H 8 B8 7 A7 2 D6
O 6 B9 7 A8 2 D7
Cu 10 B10 6 A9 7 D8
H 5 B11 6 A10 7 D9
H 4 B12 3 A11 2 D10
O 3 B13 4 A12 5 D11
H 14 B14 3 A13 4 D12
C 1 B15 2 A14 3 D13
C 16 B16 1 A15 2 D14
C 17 B17 16 A16 1 D15
C 18 B18 17 A17 16 D16
C 19 B19 18 A18 17 D17
C 20 B20 19 A19 18 D18
H 21 B21 20 A20 19 D19
H 20 B22 19 A21 18 D20
H 19 B23 18 A22 17 D21
H 18 B24 17 A23 16 D22
H 17 B25 16 A24 1 D23
C 1 B26 2 A25 3 D24
C 27 B27 1 A26 2 D25
C 28 B28 27 A27 1 D26
C 29 B29 28 A28 27 D27
C 30 B30 29 A29 28 D28
C 31 B31 30 A30 29 D29
H 32 B32 31 A31 30 D30
H 31 B33 30 A32 29 D31
H 30 B34 29 A33 28 D32
H 29 B35 28 A34 27 D33
H 28 B36 27 A35 1 D34
H 1 B37 2 A36 3 D35

B1 1.533821045
B2 1.418383106
B3 1.407714907
B4 1.405341520
B5 1.402668833
B6 1.403681610
B7 1.429832417
B8 0.991104395
B9 1.384591374
B10 2.054512851
B11 1.084951123
B12 1.087226934
B13 1.402109116
B14 0.979313533
B15 1.537885059
B16 1.413747660
B17 1.406670695
B18 1.410324051
B19 1.408097253
B20 1.409618136

B21 1.086640864
B22 1.087315852
B23 1.087120239
B24 1.087258863
B25 1.088425521
B26 1.545226845
B27 1.416550237
B28 1.404807706
B29 1.411843673
B30 1.406120421
B31 1.412833621
B32 1.086596368
B33 1.086795009
B34 1.086689530
B35 1.086955410
B36 1.087977741
B37 1.095800573
A1 119.2511557
A2 122.1703248
A3 120.3558606
A4 119.3590482
A5 115.3649807
A6 123.9189525
A7 114.9441111
A8 118.2449942
A9 122.1988154
A10 119.5115827
A11 119.9965686
A12 121.7555926
A13 112.4086080
A14 112.7949011
A15 118.5583120
A16 120.9336686
A17 120.0778721
A18 119.4220126
A19 120.2883829
A20 119.0477809
A21 120.0294429
A22 120.2738941
A23 119.8609858
A24 119.4933383
A25 113.1540459
A26 118.5150136
A27 120.8873219
A28 120.2121619
A29 119.4747388
A30 120.2780641
A31 119.3190799
A32 120.1952391
A33 120.2185477
A34 119.8153423
A35 119.4134918
A36 104.8403671
D1 179.0450438
D2 -0.482703439
D3 0.259148735
D4 0.269443045

D5 179.1118156
D6 10.23023856
D7 179.1745662
D8 -0.253097048
D9 179.9926812
D10 179.7447409
D11 179.2676093
D12 1.904269137
D13 -85.49031304
D14 148.8247882
D15 178.9369035
D16 -0.003486158
D17 0.138591884
D18 -0.118221853
D19 179.3184426
D20 179.7550429
D21 179.8234461
D22 179.6916273
D23 -1.316591444
D24 143.9840869
D25 -70.13314607
D26 -179.4900784
D27 -0.002602064
D28 0.184781744
D29 -0.120214523
D30 178.1631789
D31 179.5672715
D32 179.8686604
D33 179.7380205
D34 0.231276933
D35 29.32330665

1 2 1 16 1 27 1 38 1
2 3 1 7 2 1 1
3 4 2 2 1 14 1
4 3 2 5 1 13 1
5 6 2 4 1 12 1
6 7 1 5 2 10 1
7 2 2 6 1 8 1
8 7 1 9 1
9 8 1
10 6 1 11 1
11 10 1
12 5 1
13 4 1
14 3 1 15 1
15 14 1
16 1 1 17 1 21 2
17 16 1 18 2 26 1
18 17 2 19 1 25 1
19 18 1 20 2 24 1
20 19 2 21 1 23 1
21 20 1 16 2 22 1
22 21 1
23 20 1
24 19 1
25 18 1

```

26 17 1
27 1 1 28 2 32 1
28 27 2 29 1 37 1
29 28 1 30 2 36 1
30 29 2 31 1 35 1
31 30 1 32 2 34 1
32 31 2 27 1 33 1
33 32 1
34 31 1
35 30 1
36 29 1
37 28 1
38 1 1

```

Pb(II) Product Binding Site

input.xyz

```

C      0.00000000  0.00000000  0.00000000
C      1.40255500 -0.41272100  0.47166300
C      1.53837400 -1.16811500  1.66320000
C      2.79013800 -1.58846700  2.15364600
C      3.95813100 -1.26146200  1.44718300
C      3.85934800 -0.52188300  0.26137400
C      2.59191000 -0.10745600 -0.22054200
O      2.53418300  0.61370800 -1.41247600
H      1.98015486  0.93691660 -2.42054113
O      4.96851300 -0.16763200 -0.48774600
Pb     4.74604783  0.18867898 -1.93685318
H      4.93330300 -1.57548000  1.80681400
H      2.85442600 -2.16459400  3.07319900
O      0.35411000 -1.48240900  2.34862600
H      0.52576900 -1.99072300  3.16801900
C     -0.56971500 -0.97131800 -1.04620800
C     -1.80947600 -1.60145000 -0.79747400
C     -2.36903300 -2.50072600 -1.72775700
C     -1.69153700 -2.78393800 -2.92956300
C     -0.45501300 -2.15748100 -3.18988300
C      0.09981600 -1.25921800 -2.25906900
H      1.04683400 -0.77433200 -2.47377500
H      0.07422900 -2.36693800 -4.11687200
H     -2.11791400 -3.47819900 -3.64972800
H     -3.32339300 -2.97629900 -1.51390800
H     -2.34007100 -1.39080600  0.12904300
C     -0.11262900  1.49318200 -0.37466600
C      0.41823600  2.46330900  0.50829900
C      0.26497500  3.83765300  0.25489000
C     -0.43286400  4.27420800 -0.89098100
C     -0.97306700  3.31778100 -1.77120200
C     -0.81593800  1.94033700 -1.51243700
H     -1.23987100  1.21887600 -2.20436200
H     -1.51726100  3.63980800 -2.65630800
H     -0.55432500  5.33637800 -1.08954600
H      0.68323200  4.56503600  0.94708800
H      0.95628600  2.14047000  1.39750500

```

H -0.63400900 -0.11931700 0.88638600

input.com

%NProcShared=2

#N B3LYP/LANL2DZ OPT SCRF=(PCM,Solvent=Water) UHF Geom=Connectivity

11/27 Binding Site 4a Lead Adsorbed

1 1

C

C 1 B1

C 2 B2 1 A1

C 3 B3 2 A2 1 D1

C 4 B4 3 A3 2 D2

C 5 B5 4 A4 3 D3

C 2 B6 3 A5 4 D4

O 7 B7 2 A6 3 D5

H 8 B8 7 A7 2 D6

O 6 B9 7 A8 2 D7

Pb 10 B10 6 A9 7 D8

H 5 B11 6 A10 7 D9

H 4 B12 3 A11 2 D10

O 3 B13 4 A12 5 D11

H 14 B14 3 A13 4 D12

C 1 B15 2 A14 3 D13

C 16 B16 1 A15 2 D14

C 17 B17 16 A16 1 D15

C 18 B18 17 A17 16 D16

C 19 B19 18 A18 17 D17

C 20 B20 19 A19 18 D18

H 21 B21 20 A20 19 D19

H 20 B22 19 A21 18 D20

H 19 B23 18 A22 17 D21

H 18 B24 17 A23 16 D22

H 17 B25 16 A24 1 D23

C 1 B26 2 A25 3 D24

C 27 B27 1 A26 2 D25

C 28 B28 27 A27 1 D26

C 29 B29 28 A28 27 D27

C 30 B30 29 A29 28 D28

C 31 B31 30 A30 29 D29

H 32 B32 31 A31 30 D30

H 31 B33 30 A32 29 D31

H 30 B34 29 A33 28 D32

H 29 B35 28 A34 27 D33

H 28 B36 27 A35 1 D34

H 1 B37 2 A36 3 D35

B1 1.536217803

B2 1.417331055

B3 1.408597244

B4 1.403648777

B5 1.401027538

B6 1.409574332

B7 1.394315811

B8 1.194824791
B9 1.384529358
B10 1.508761044
B11 1.085772624
B12 1.087029432
B13 1.403948269
B14 0.979415552
B15 1.537070271
B16 1.412778212
B17 1.409690683
B18 1.408384723
B19 1.410392313
B20 1.407524898
B21 1.085382970
B22 1.087785795
B23 1.087397494
B24 1.087521992
B25 1.088271887
B26 1.543584267
B27 1.415129406
B28 1.405889927
B29 1.410879118
B30 1.407608218
B31 1.410319404
B32 1.085810927
B33 1.087778070
B34 1.087375714
B35 1.087732972
B36 1.088306084
B37 1.096304748
A1 119.2613169
A2 122.4740816
A3 119.6500888
A4 119.3602551
A5 116.5774901
A6 119.7933609
A7 151.6835451
A8 117.2211554
A9 117.5145458
A10 119.7578952
A11 120.3483209
A12 120.8514757
A13 112.1349489
A14 112.1854554
A15 119.1617721
A16 121.1090358
A17 120.0304756
A18 119.3356289
A19 120.4640642
A20 119.8824956
A21 119.8886346
A22 120.3252224
A23 119.8368058
A24 119.4331855
A25 113.6425042
A26 118.9689381
A27 121.1176465

A28 120.1846845
A29 119.1732070
A30 120.4068937
A31 119.2443664
A32 119.9777988
A33 120.3848958
A34 119.8075077
A35 119.4656529
A36 104.5081411
D1 179.6485455
D2 -0.263216261
D3 -0.092597097
D4 0.673643974
D5 178.9485646
D6 -30.20175239
D7 -179.7328190
D8 -20.52657938
D9 179.8953381
D10 179.8382715
D11 179.9269631
D12 0.814627941
D13 -96.13738168
D14 123.2457735
D15 -179.9128681
D16 -0.038084934
D17 -0.145608394
D18 0.087291946
D19 -179.3484999
D20 -179.7801905
D21 179.8906721
D22 179.8297616
D23 -0.065257674
D24 131.6001352
D25 -47.24069085
D26 -175.8642208
D27 0.321205638
D28 0.122142550
D29 -0.146546262
D30 -179.9649551
D31 179.7346057
D32 179.9292069
D33 -179.8924008
D34 4.276795393
D35 17.66507967

1 2 1 16 1 27 1 38 1
2 3 1 7 2 1 1
3 4 2 2 1 14 1
4 3 2 5 1 13 1
5 6 2 4 1 12 1
6 7 1 5 2 10 1
7 2 2 6 1 8 1
8 7 1 9 1
9 8 1
10 6 1 11 1
11 10 1
12 5 1

```

13 4 1
14 3 1 15 1
15 14 1
16 1 1 17 1 21 2
17 16 1 18 2 26 1
18 17 2 19 1 25 1
19 18 1 20 2 24 1
20 19 2 21 1 23 1
21 20 1 16 2 22 1
22 21 1
23 20 1
24 19 1
25 18 1
26 17 1
27 1 1 28 2 32 1
28 27 2 29 1 37 1
29 28 1 30 2 36 1
30 29 2 31 1 35 1
31 30 1 32 2 34 1
32 31 2 27 1 33 1
33 32 1
34 31 1
35 30 1
36 29 1
37 28 1
38 1 1

```

K+

input.xyz

```
K      0.00000000  0.00000000  0.00000000
```

input.com

```
#N B3LYP/LANL2DZ OPT SCRF=(PCM,Solvent=Water) UHF Geom=Connectivity
```

```
Potassium Ion (+1)
```

```
1 1
K
```

```
1
```

Binding Site 6 Input Files***Cu(II)***

input.xyz

```
Cu    0.00000000  0.00000000  0.00000000
```

input.com

```
#N B3LYP/LANL2DZ OPT SCRF=(PCM,Solvent=Water) UHF Geom=Connectivity
```

```
Copper Ion (2+)
```

```
2 2
```

```
Cu
```

```
1
```

Pb(II)

input.xyz

```
Pb    0.00000000  0.00000000  0.00000000
```

input.com

```
#N B3LYP/LANL2DZ OPT SCRF=(PCM,Solvent=Water) UHF Geom=Connectivity
```

```
Lead Ion (+2)
```

```
2 1
```

```
Pb
```

```
1
```

Reactant Binding Site

input.xyz

```
C    0.00000000  0.00000000  0.00000000
C   -0.64699100 -0.11053300 -1.34153400
C   -1.79400300 -0.70609700 -1.81391800
C   -1.87533000 -0.45360400 -3.24550300
C   -2.97391900 -0.90834200 -4.18337600
C   -3.08315800 -2.42103300 -4.24778600
C   -4.17696600 -3.20726500 -4.06214000
C   -5.54664500 -2.85192200 -3.73958300
C   -6.65944900 -3.64509100 -3.55077900
C   -7.77136200 -2.78878200 -3.20988000
C   -7.29980200 -1.47693300 -3.23527900
```

```

O   -5.93521700 -1.50221200 -3.55917500
C   -7.90933300 -0.16373600 -3.12966900
C   -7.29309500  1.00933600 -2.69133200
C   -5.93300300  1.33998400 -2.18046400
H   -5.39783100  0.42977200 -1.90187300
H   -5.34075600  1.86160000 -2.94443300
H   -6.00273000  1.99828400 -1.30707600
O   -8.20350600  2.05551400 -2.76318500
C   -9.42154100  1.53822600 -3.25716600
C   -9.26159400  0.18564700 -3.48691400
H   -10.0105880 -0.48149400 -3.88619300
C   -10.5484860  2.45731300 -3.43263700
C   -11.8371140  1.85860000 -3.96799700
H   -12.5992990  2.63868200 -4.03422300
H   -11.6796080  1.42592100 -4.96375400
H   -12.1981940  1.05737800 -3.31181600
O   -10.4488720  3.68454600 -3.15312500
C   -9.12386500 -3.32342300 -2.93373500
O   -9.53828700 -4.35043100 -3.55601100
C   -9.97320400 -2.71633400 -1.90768700
O   -9.41082700 -1.80880700 -0.98748100
C   -10.4261470 -1.43316600 -0.11778300
C   -11.6034090 -2.07272600 -0.45763700
C   -11.3126220 -2.89799900 -1.59701900
H   -11.9989310 -3.53968300 -2.12906900
H   -12.5535750 -1.96726100  0.04379900
H   -10.1545570 -0.73722400  0.66014200
H   -6.69449700 -4.72224900 -3.61496800
H   -4.04650700 -4.28379900 -4.16626600
H   -2.14902000 -2.93322100 -4.48236100
H   -3.93014500 -0.47070600 -3.88715400
H   -2.74972500 -0.53351800 -5.19344200
C   -0.76403200  0.28646800 -3.56895200
H   -0.38824200  0.70685700 -4.48844700
O    0.01349700  0.51595200 -2.41795900
H   -2.50513800 -1.26325100 -1.22034800
H   -0.60581300 -0.51954800  0.74869200
H    0.10360900  1.04799100  0.31021800
H    1.00251100 -0.44748400 -0.00008100

```

input.com

```

%NProcShared=2
#N B3LYP/LANL2DZ OPT SCRF=(PCM,Solvent=Water) UHF Geom=Connectivity

```

11/22 Binding Site 6

```

O 1
C
C 1 B1
C 2 B2 1 A1
C 3 B3 2 A2 1 D1
C 4 B4 3 A3 2 D2
C 5 B5 4 A4 3 D3
C 6 B6 5 A5 4 D4
C 7 B7 6 A6 5 D5

```

C 8 B8 7 A7 6 D6
 C 9 B9 8 A8 7 D7
 C 10 B10 9 A9 8 D8
 O 8 B11 9 A10 10 D9
 C 11 B12 10 A11 9 D10
 C 13 B13 11 A12 10 D11
 C 14 B14 13 A13 11 D12
 H 15 B15 14 A14 13 D13
 H 15 B16 14 A15 13 D14
 H 15 B17 14 A16 13 D15
 O 14 B18 13 A17 11 D16
 C 19 B19 14 A18 13 D17
 C 13 B20 11 A19 10 D18
 H 21 B21 13 A20 11 D19
 C 20 B22 21 A21 13 D20
 C 23 B23 20 A22 21 D21
 H 24 B24 23 A23 20 D22
 H 24 B25 23 A24 20 D23
 H 24 B26 23 A25 20 D24
 O 23 B27 20 A26 21 D25
 C 10 B28 11 A27 12 D26
 O 29 B29 10 A28 11 D27
 C 29 B30 10 A29 11 D28
 O 31 B31 29 A30 10 D29
 C 32 B32 31 A31 29 D30
 C 33 B33 32 A32 31 D31
 C 31 B34 29 A33 10 D32
 H 35 B35 31 A34 29 D33
 H 34 B36 33 A35 32 D34
 H 33 B37 32 A36 31 D35
 H 9 B38 10 A37 11 D36
 H 7 B39 8 A38 9 D37
 H 6 B40 7 A39 8 D38
 H 5 B41 6 A40 7 D39
 H 5 B42 6 A41 7 D40
 C 4 B43 5 A42 6 D41
 H 44 B44 4 A43 5 D42
 O 44 B45 4 A44 5 D43
 H 3 B46 4 A45 5 D44
 H 1 B47 2 A46 3 D45
 H 1 B48 2 A47 3 D46
 H 1 B49 2 A48 3 D47

B1 1.493495354
 B2 1.376037663
 B3 1.455954123
 B4 1.514361319
 B5 1.517997322
 B6 1.359794520
 B7 1.451320857
 B8 1.379527729
 B9 1.444239506
 B10 1.394260285
 B11 1.416069324
 B12 1.451608719
 B13 1.395702875
 B14 1.490021631

B15 1.092020100
B16 1.098402655
B17 1.095913931
B18 1.388704234
B19 1.412520217
B20 1.441631813
B21 1.079579939
B22 1.464758007
B23 1.518430014
B24 1.092629756
B25 1.097064839
B26 1.096772066
B27 1.262596825
B28 1.480324770
B29 1.270322182
B30 1.463799265
B31 1.409486512
B32 1.388652395
B33 1.382202428
B34 1.386923703
B35 1.079747934
B36 1.079525987
B37 1.078547032
B38 1.079637878
B39 1.089397644
B40 1.090860111
B41 1.092538743
B42 1.100449592
B43 1.373793676
B44 1.078617676
B45 1.407834912
B46 1.080952780
B47 1.094293940
B48 1.097841140
B49 1.097848005
A1 134.5474091
A2 108.0019775
A3 126.6839101
A4 112.1923602
A5 128.9226909
A6 130.3848210
A7 130.6112287
A8 108.2066703
A9 107.0482928
A10 108.0128009
A11 135.0591033
A12 126.7124889
A13 134.2039557
A14 110.4779124
A15 111.0440197
A16 110.3932905
A17 109.1155377
A18 107.9100919
A19 126.5186722
A20 126.3458913
A21 133.1264928
A22 116.6002349

A23 109.3816927
A24 110.7128054
A25 110.8854696
A26 121.5116252
A27 130.7096910
A28 119.9122413
A29 120.7369795
A30 119.5480489
A31 106.9374964
A32 110.0956254
A33 131.5322948
A34 125.5430743
A35 126.1748575
A36 116.2417139
A37 125.4922077
A38 112.0991056
A39 116.5324343
A40 110.3459716
A41 108.3689169
A42 127.0695705
A43 133.8281896
A44 110.0038167
A45 126.3392250
A46 109.8523923
A47 111.4292843
A48 111.4293504
D1 179.9445484
D2 -179.4697631
D3 -61.63907469
D4 127.1776727
D5 -0.637544495
D6 179.9723841
D7 178.3469509
D8 1.478906550
D9 -1.473441031
D10 172.3388855
D11 154.5406633
D12 -1.798166974
D13 -15.23109833
D14 104.5784568
D15 -136.0944693
D16 178.7668524
D17 -0.029527563
D18 -26.97462395
D19 -0.174019833
D20 179.5988920
D21 0.355093227
D22 178.9452978
D23 -60.83624763
D24 58.50874189
D25 -179.5709648
D26 -179.5928518
D27 144.7907616
D28 -37.83660711
D29 -13.41043587
D30 -178.1080506
D31 0.074545779

D32 169.4618267
D33 -2.555729915
D34 -179.8461781
D35 179.6515381
D36 179.7714094
D37 0.154786017
D38 179.7964675
D39 3.764990957
D40 -112.9699159
D41 118.9280705
D42 -0.509606769
D43 179.4565395
D44 0.588210746
D45 -0.201193397
D46 -120.0832282
D47 119.6753245

1 2 1 48 1 49 1 50 1
2 3 2 46 1 1 1
3 4 1 47 1 2 2
4 5 1 3 1 44 2
5 6 1 42 1 43 1 4 1
6 7 2 41 1 5 1
7 8 1 40 1 6 2
8 9 2 12 1 7 1
9 10 1 39 1 8 2
10 11 2 9 1 29 1
11 10 2 12 1 13 1
12 8 1 11 1
13 11 1 14 2 21 1
14 13 2 15 1 19 1
15 14 1 16 1 17 1 18 1
16 15 1
17 15 1
18 15 1
19 20 1 14 1
20 21 2 19 1 23 1
21 13 1 20 2 22 1
22 21 1
23 20 1 24 1 28 2
24 23 1 25 1 26 1 27 1
25 24 1
26 24 1
27 24 1
28 23 2
29 10 1 30 2 31 1
30 29 2
31 29 1 32 1 35 2
32 31 1 33 1
33 32 1 34 2 38 1
34 33 2 35 1 37 1
35 31 2 34 1 36 1
36 35 1
37 34 1
38 33 1
39 9 1
40 7 1

```

41 6 1
42 5 1
43 5 1
44 4 2 45 1 46 1
45 44 1
46 44 1 2 1
47 3 1
48 1 1
49 1 1
50 1 1

```

Cu(II) Product Binding Site

input.xyz

```

C      0.00000000  0.00000000  0.00000000
C     -0.64699100 -0.11053300 -1.34153400
C     -1.79400300 -0.70609700 -1.81391800
C     -1.87533000 -0.45360400 -3.24550300
C     -2.97391900 -0.90834200 -4.18337600
C     -3.08315800 -2.42103300 -4.24778600
C     -4.17696600 -3.20726500 -4.06214000
C     -5.54664500 -2.85192200 -3.73958300
C     -6.65944900 -3.64509100 -3.55077900
C     -7.77136200 -2.78878200 -3.20988000
C     -7.29980200 -1.47693300 -3.23527900
O     -5.93521700 -1.50221200 -3.55917500
C     -7.90933300 -0.16373600 -3.12966900
C     -7.29309500  1.00933600 -2.69133200
C     -5.93300300  1.33998400 -2.18046400
H     -5.39783100  0.42977200 -1.90187300
H     -5.34075600  1.86160000 -2.94443300
H     -6.00273000  1.99828400 -1.30707600
O     -8.20350600  2.05551400 -2.76318500
C     -9.42154100  1.53822600 -3.25716600
C     -9.26159400  0.18564700 -3.48691400
H    -10.0105880 -0.48149400 -3.88619300
C    -10.5484860  2.45731300 -3.43263700
C    -11.8371140  1.85860000 -3.96799700
H    -12.5992990  2.63868200 -4.03422300
H    -11.6796080  1.42592100 -4.96375400
H    -12.1981940  1.05737800 -3.31181600
O    -10.4488720  3.68454600 -3.15312500
C    -9.12386500 -3.32342300 -2.93373500
O    -9.53828700 -4.35043100 -3.55601100
C    -9.97320400 -2.71633400 -1.90768700
O    -9.41082700 -1.80880700 -0.98748100
C    -10.4261470 -1.43316600 -0.11778300
C    -11.6034090 -2.07272600 -0.45763700
C    -11.3126220 -2.89799900 -1.59701900
H    -11.9989310 -3.53968300 -2.12906900
H    -12.5535750 -1.96726100  0.04379900
H    -10.1545570 -0.73722400  0.66014200
H    -6.69449700 -4.72224900 -3.61496800
H    -4.04650700 -4.28379900 -4.16626600

```

```

H   -2.14902000 -2.93322100 -4.48236100
H   -3.93014500 -0.47070600 -3.88715400
H   -2.74972500 -0.53351800 -5.19344200
C   -0.76403200  0.28646800 -3.56895200
H   -0.38824200  0.70685700 -4.48844700
O    0.01349700  0.51595200 -2.41795900
H   -2.50513800 -1.26325100 -1.22034800
H   -0.60581300 -0.51954800  0.74869200
H    0.10360900  1.04799100  0.31021800
H    1.00251100 -0.44748400 -0.00008100
Cu   -8.19950339  4.28852258 -2.56116562

```

input.com

```

%NProcShared=2
#N B3LYP/LANL2DZ OPT SCRF=(PCM,Solvent=Water) UHF Geom=Connectivity

6 Copper config 3

2 2
C
C 1 B1
C 2 B2 1 A1
C 3 B3 2 A2 1 D1
C 4 B4 3 A3 2 D2
C 5 B5 4 A4 3 D3
C 6 B6 5 A5 4 D4
C 7 B7 6 A6 5 D5
C 8 B8 7 A7 6 D6
C 9 B9 8 A8 7 D7
C 10 B10 9 A9 8 D8
O 8 B11 9 A10 10 D9
C 11 B12 10 A11 9 D10
C 13 B13 11 A12 10 D11
C 14 B14 13 A13 11 D12
H 15 B15 14 A14 13 D13
H 15 B16 14 A15 13 D14
H 15 B17 14 A16 13 D15
O 14 B18 13 A17 11 D16
C 19 B19 14 A18 13 D17
C 13 B20 11 A19 10 D18
H 21 B21 13 A20 11 D19
C 20 B22 21 A21 13 D20
C 23 B23 20 A22 21 D21
H 24 B24 23 A23 20 D22
H 24 B25 23 A24 20 D23
H 24 B26 23 A25 20 D24
O 23 B27 20 A26 21 D25
C 10 B28 11 A27 12 D26
O 29 B29 10 A28 11 D27
C 29 B30 10 A29 11 D28
O 31 B31 29 A30 10 D29
C 32 B32 31 A31 29 D30
C 33 B33 32 A32 31 D31
C 31 B34 29 A33 10 D32
H 35 B35 31 A34 29 D33

```

H 34 B36 33 A35 32 D34
H 33 B37 32 A36 31 D35
H 9 B38 10 A37 11 D36
H 7 B39 8 A38 9 D37
H 6 B40 7 A39 8 D38
H 5 B41 6 A40 7 D39
H 5 B42 6 A41 7 D40
C 4 B43 5 A42 6 D41
H 44 B44 4 A43 5 D42
O 44 B45 4 A44 5 D43
H 3 B46 4 A45 5 D44
H 1 B47 2 A46 3 D45
H 1 B48 2 A47 3 D46
H 1 B49 2 A48 3 D47
Cu 1 B50 2 A49 3 D48

B1 1.493495354
B2 1.376037663
B3 1.455954123
B4 1.514361319
B5 1.517997322
B6 1.359794520
B7 1.451320857
B8 1.379527729
B9 1.444239506
B10 1.394260285
B11 1.416069324
B12 1.451608719
B13 1.395702875
B14 1.490021631
B15 1.092020100
B16 1.098402655
B17 1.095913931
B18 1.388704234
B19 1.412520217
B20 1.441631813
B21 1.079579939
B22 1.464758007
B23 1.518430014
B24 1.092629756
B25 1.097064839
B26 1.096772066
B27 1.262596825
B28 1.480324770
B29 1.270322182
B30 1.463799265
B31 1.409486512
B32 1.388652395
B33 1.382202428
B34 1.386923703
B35 1.079747934
B36 1.079525987
B37 1.078547032
B38 1.079637878
B39 1.089397644
B40 1.090860111
B41 1.092538743

B42 1.100449592
B43 1.373793676
B44 1.078617676
B45 1.407834912
B46 1.080952780
B47 1.094293940
B48 1.097841140
B49 1.097848005
B50 9.601190086
A1 134.5474091
A2 108.0019775
A3 126.6839101
A4 112.1923602
A5 128.9226909
A6 130.3848210
A7 130.6112287
A8 108.2066703
A9 107.0482928
A10 108.0128009
A11 135.0591033
A12 126.7124889
A13 134.2039557
A14 110.4779124
A15 111.0440197
A16 110.3932905
A17 109.1155377
A18 107.9100919
A19 126.5186722
A20 126.3458913
A21 133.1264928
A22 116.6002349
A23 109.3816927
A24 110.7128054
A25 110.8854696
A26 121.5116252
A27 130.7096910
A28 119.9122413
A29 120.7369795
A30 119.5480489
A31 106.9374964
A32 110.0956254
A33 131.5322948
A34 125.5430743
A35 126.1748575
A36 116.2417139
A37 125.4922077
A38 112.0991056
A39 116.5324343
A40 110.3459716
A41 108.3689169
A42 127.0695705
A43 133.8281896
A44 110.0038167
A45 126.3392250
A46 109.8523923
A47 111.4292843
A48 111.4293504

A49 54.79404600
D1 179.9445484
D2 -179.4697631
D3 -61.63907469
D4 127.1776727
D5 -0.637544495
D6 179.9723841
D7 178.3469509
D8 1.478906550
D9 -1.473441031
D10 172.3388855
D11 154.5406633
D12 -1.798166974
D13 -15.23109833
D14 104.5784568
D15 -136.0944693
D16 178.7668524
D17 -0.029527563
D18 -26.97462395
D19 -0.174019833
D20 179.5988920
D21 0.355093227
D22 178.9452978
D23 -60.83624763
D24 58.50874189
D25 -179.5709648
D26 -179.5928518
D27 144.7907616
D28 -37.83660711
D29 -13.41043587
D30 -178.1080506
D31 0.074545779
D32 169.4618267
D33 -2.555729915
D34 -179.8461781
D35 179.6515381
D36 179.7714094
D37 0.154786017
D38 179.7964675
D39 3.764990957
D40 -112.9699159
D41 118.9280705
D42 -0.509606769
D43 179.4565395
D44 0.588210746
D45 -0.201193397
D46 -120.0832282
D47 119.6753245
D48 -69.31437367

1 2 1 48 1 49 1 50 1
2 3 2 46 1 1 1
3 4 1 47 1 2 2
4 5 1 3 1 44 2
5 6 1 42 1 43 1 4 1
6 7 2 41 1 5 1
7 8 1 40 1 6 2

```

8 9 2 12 1 7 1
9 10 1 39 1 8 2
10 11 2 9 1 29 1
11 10 2 12 1 13 1
12 8 1 11 1
13 11 1 14 2 21 1
14 13 2 15 1 19 1
15 14 1 16 1 17 1 18 1
16 15 1
17 15 1
18 15 1
19 20 1 14 1
20 21 2 19 1 23 1
21 13 1 20 2 22 1
22 21 1
23 20 1 24 1 28 2
24 23 1 25 1 26 1 27 1
25 24 1
26 24 1
27 24 1
28 23 2
29 10 1 30 2 31 1
30 29 2
31 29 1 32 1 35 2
32 31 1 33 1
33 32 1 34 2 38 1
34 33 2 35 1 37 1
35 31 2 34 1 36 1
36 35 1
37 34 1
38 33 1
39 9 1
40 7 1
41 6 1
42 5 1
43 5 1
44 4 2 45 1 46 1
45 44 1
46 44 1 2 1
47 3 1
48 1 1
49 1 1
50 1 1
51

```

Pb(II) Product Binding Site

input.xyz

```

C      0.00000000  0.00000000  0.00000000
C     -0.57428800 -0.28682400 -1.34734200
C     -1.64098400 -1.02347700 -1.80730600
C     -1.67662800 -0.89620100 -3.25623300
C     -2.68894800 -1.51911100 -4.19448000
C     -2.62048200 -3.01969300 -4.14219900

```

```

C   -3.64568000 -3.93649500 -3.95181400
C   -5.01824600 -3.70297700 -3.71197300
C   -6.07630700 -4.63854800 -3.57822100
C   -7.26543500 -3.93412000 -3.34127300
C   -6.93762400 -2.54723300 -3.35056500
O   -5.56472700 -2.41387100 -3.56796100
C   -7.70555900 -1.34664100 -3.26185500
C   -7.20071800 -0.05191200 -3.00948200
C   -5.85559300  0.51071000 -2.73921400
H   -5.22425700 -0.21799400 -2.22631500
H   -5.36016300  0.78384100 -3.68151000
H   -5.93647700  1.41407800 -2.12770400
O   -8.26262500  0.82984600 -3.01674900
C   -9.46020500  0.10072400 -3.28684600
C   -9.13739000 -1.22495300 -3.42959200
H   -9.83192800 -2.01833600 -3.65920100
C   -10.6778420  0.89683400 -3.35087100
C   -11.9895180  0.23698900 -3.65704400
H   -12.7945350  0.97045500 -3.58431500
H   -11.9756740 -0.18317500 -4.67100300
H   -12.1825320 -0.58874500 -2.96254600
O   -10.6001990  2.15612300 -3.14787900
C   -8.58186900 -4.62894400 -3.14616500
O   -8.89839600 -5.56693200 -3.93047200
C   -9.41935800 -4.25639500 -2.02118000
O   -8.92841600 -3.30725400 -1.09778900
C   -9.89660400 -3.16634600 -0.11566600
C   -10.9748480 -3.99100500 -0.38626500
C   -10.6703390 -4.68991200 -1.59991700
H   -11.2875010 -5.41734000 -2.10601700
H   -11.8696580 -4.08366500  0.20994500
H   -9.67468000 -2.47044800  0.67796800
H   -5.96978500 -5.71205800 -3.63205900
H   -3.38690300 -4.99148800 -4.00126800
H   -1.62624500 -3.44116600 -4.28866600
H   -3.69664300 -1.15866300 -3.98648400
H   -2.44658700 -1.21957700 -5.22674200
C   -0.61950900 -0.08743700 -3.60375300
H   -0.24398000  0.28605900 -4.54324000
O   0.07474100  0.30529300 -2.45275300
H   -2.32838700 -1.58829100 -1.19374600
H   -0.58606400 -0.51007100  0.77028800
H   -0.00869900  1.07578200  0.21762400
H   1.03897600 -0.34632300  0.07354100
Pb  -8.85320300  3.03198100 -2.72493100

```

input.com

```

%NProcShared=2
#N B3LYP/LANL2DZ OPT SCRF=(PCM,Solvent=Water) UHF Geom=Connectivity

6 Lead config 3

2 1
C
C 1 B1

```

C 2 B2 1 A1
 C 3 B3 2 A2 1 D1
 C 4 B4 3 A3 2 D2
 C 5 B5 4 A4 3 D3
 C 6 B6 5 A5 4 D4
 C 7 B7 6 A6 5 D5
 C 8 B8 7 A7 6 D6
 C 9 B9 8 A8 7 D7
 C 10 B10 9 A9 8 D8
 O 8 B11 9 A10 10 D9
 C 11 B12 10 A11 9 D10
 C 13 B13 11 A12 10 D11
 C 14 B14 13 A13 11 D12
 H 15 B15 14 A14 13 D13
 H 15 B16 14 A15 13 D14
 H 15 B17 14 A16 13 D15
 O 14 B18 13 A17 11 D16
 C 19 B19 14 A18 13 D17
 C 13 B20 11 A19 10 D18
 H 21 B21 13 A20 11 D19
 C 20 B22 21 A21 13 D20
 C 23 B23 20 A22 21 D21
 H 24 B24 23 A23 20 D22
 H 24 B25 23 A24 20 D23
 H 24 B26 23 A25 20 D24
 O 23 B27 20 A26 21 D25
 C 10 B28 11 A27 12 D26
 O 29 B29 10 A28 11 D27
 C 29 B30 10 A29 11 D28
 O 31 B31 29 A30 10 D29
 C 32 B32 31 A31 29 D30
 C 33 B33 32 A32 31 D31
 C 31 B34 29 A33 10 D32
 H 35 B35 31 A34 29 D33
 H 34 B36 33 A35 32 D34
 H 33 B37 32 A36 31 D35
 H 9 B38 10 A37 11 D36
 H 7 B39 8 A38 9 D37
 H 6 B40 7 A39 8 D38
 H 5 B41 6 A40 7 D39
 H 5 B42 6 A41 7 D40
 C 4 B43 5 A42 6 D41
 H 44 B44 4 A43 5 D42
 O 44 B45 4 A44 5 D43
 H 3 B46 4 A45 5 D44
 H 1 B47 2 A46 3 D45
 H 1 B48 2 A47 3 D46
 H 1 B49 2 A48 3 D47
 Pb 1 B50 2 A49 3 D48

B1 1.492449389
 B2 1.375523493
 B3 1.454942998
 B4 1.514303828
 B5 1.503052639
 B6 1.388453562
 B7 1.412795734

B8 1.418688046
B9 1.402279773
B10 1.425132255
B11 1.407542262
B12 1.427940748
B13 1.412402120
B14 1.482885556
B15 1.092089762
B16 1.099078332
B17 1.093874054
B18 1.380288541
B19 1.427854732
B20 1.446749350
B21 1.079147771
B22 1.456204037
B23 1.499877081
B24 1.091473431
B25 1.097653086
B26 1.096092384
B27 1.277905698
B28 1.501281452
B29 1.262991805
B30 1.451127780
B31 1.412283125
B32 1.386293135
B33 1.384159098
B34 1.389371429
B35 1.079897050
B36 1.079229899
B37 1.078600581
B38 1.080124616
B39 1.087392047
B40 1.089770290
B41 1.090245069
B42 1.101827713
B43 1.375634377
B44 1.078497619
B45 1.400364565
B46 1.080737532
B47 1.094069029
B48 1.097607758
B49 1.097642486
B50 9.746658971
A1 134.6847227
A2 107.7677327
A3 126.6854038
A4 111.0186604
A5 129.0762902
A6 129.1598625
A7 129.1660118
A8 108.4870846
A9 107.0199524
A10 107.7441466
A11 133.9565996
A12 126.1294472
A13 134.7968422
A14 110.9054484

A15 110.2990272
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A18 108.6659853
A19 126.5670618
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A21 136.0943743
A22 119.9810767
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A24 110.2389891
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A27 130.7641873
A28 118.8670147
A29 119.2093200
A30 118.6067308
A31 106.7823743
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A33 132.4228097
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A35 126.0879349
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A40 111.4405016
A41 107.0959410
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A43 133.7285116
A44 109.7682025
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A46 109.8695888
A47 111.3648756
A48 111.3508068
A49 57.17115072
D1 179.7078556
D2 -179.1280968
D3 -63.21248703
D4 128.8104909
D5 -2.365386034
D6 176.7859143
D7 179.7390882
D8 0.909824425
D9 -0.526406856
D10 175.0177764
D11 165.8885564
D12 -1.511701766
D13 -30.26738998
D14 89.25035678
D15 -151.6070131
D16 179.4044935
D17 -0.481881871
D18 -14.96173094
D19 -0.916438469
D20 179.0125626
D21 -0.853772125
D22 175.4953015

D23 -64.32889437
D24 54.46745778
D25 179.4396866
D26 179.7770810
D27 134.0420765
D28 -49.34855723
D29 -3.868705728
D30 -178.2533707
D31 0.063019707
D32 178.6527467
D33 -2.209925028
D34 -179.9420157
D35 179.8569931
D36 179.7933366
D37 -2.384880023
D38 178.5803371
D39 4.097223972
D40 -112.5938513
D41 117.5646634
D42 -0.658870970
D43 179.0870556
D44 0.537406709
D45 0.144135827
D46 -119.7807422
D47 120.0350733
D48 -65.25681909

1 2 1 48 1 49 1 50 1
2 3 2 46 1 1 1
3 4 1 47 1 2 2
4 5 1 3 1 44 2
5 6 1 42 1 43 1 4 1
6 7 2 41 1 5 1
7 8 1 40 1 6 2
8 9 2 12 1 7 1
9 10 1 39 1 8 2
10 11 2 9 1 29 1
11 10 2 12 1 13 1
12 8 1 11 1
13 11 1 14 2 21 1
14 13 2 15 1 19 1
15 14 1 16 1 17 1 18 1
16 15 1
17 15 1
18 15 1
19 20 1 14 1
20 21 2 19 1 23 1
21 13 1 20 2 22 1
22 21 1
23 20 1 24 1 28 2
24 23 1 25 1 26 1 27 1
25 24 1
26 24 1
27 24 1
28 23 2
29 10 1 30 2 31 1
30 29 2

31 29 1 32 1 35 2
32 31 1 33 1
33 32 1 34 2 38 1
34 33 2 35 1 37 1
35 31 2 34 1 36 1
36 35 1
37 34 1
38 33 1
39 9 1
40 7 1
41 6 1
42 5 1
43 5 1
44 4 2 45 1 46 1
45 44 1
46 44 1 2 1
47 3 1
48 1 1
49 1 1
50 1 1
51