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Quantum Chemical Calculations of the Redox Potential of the Pu(VII)/Pu(VIII) Couple

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The redox potential of the Pu(VII)/Pu(VIII) couple was studied by density functional theory calculations. The spin–orbit effect was corrected at the CASSCF level. The redox potential (relative to the standard hydrogen potential) of the Pu(VII)/Pu(VIII) couple in alkaline solution was found to vary from 4.36 to 1.06 V depending on the number of Pu–O oxo bonds, coordination numbers, and coordination modes. The redox potential drops substantially as the number of Pu–O oxo bonds increases. Pu(VIII) may be synthesized in strong alkaline solution assuming that both Pu(VII) and Pu(VIII) exist in penta-oxo form, $\text{Pu}^{\text{VII}}\text{O}_5\text{OH}^{4-}$ and $\text{Pu}^{\text{VIII}}\text{O}_5\text{OH}^{3-}$, respectively. The Mulliken population of Pu in Pu(VII) and Pu(VIII) complexes are very similar, suggesting that the spin–orbit effect is rather small in Pu(VII) complexes and that when Pu(VII) is oxidized to Pu(VIII) the electron is stripped mainly from the ligand. Consequently, Pu(VIII) is in an unstable oxidation state and easily reduced back to Pu(VII) by the solvent water molecules. In acidic medium, the Pu(VII)/Pu(VIII) redox potential is too high to get the Pu(VIII) valence state.

1. Introduction

Among all of the actinide series, plutonium exhibits the most complex redox behavior in aqueous solution.¹ The common oxidation states of Pu are III, IV, V, and VI, and quite often more than two oxidation states of Pu coexist in the same solution. The redox behavior of Pu becomes further complicated at the solid–liquid interface and/or in the presence of complexing ligands and bacteria.² All of the oxidation states of Pu have characteristic absorption bands in the visible wavelength region so that each oxidation state exhibits unique color (which may change upon ligand coordination), and therefore it is visually noticeable if there is a change in the oxidation state.

The highest known oxidation state of Pu in aqueous solution is VII. But this oxidation state is known to be stable only in strong alkaline medium. From its analogy with Np(VII),^{3–5} Pu(VII) presumably exist as a tetra-oxo complex PuO_4^- , but its stoichiometry and structure are not well understood. The formal electronic configuration of a bare Pu^{7+} ion is $5f^1$, and one might speculate that an even higher oxidation state of Pu^{8+} with the $5f^0$ configuration is also attainable. Nikonov et al.⁶ and Tananaev et al.⁷ claim that, during the ozonization of Pu(VI) in strong alkaline solution, Pu(VI) is mainly oxidized to Pu(VII) but partly to Pu(VIII). Their claim of the existence of Pu(VIII) is mainly based on the observation of UV–vis absorption spectra in which they found a small unstable component that, they claim, belongs neither to Pu(VI) nor to Pu(VII). Such a component, however, can also be attributed to Pu(VII) species with increased/decreased number of Pu–O oxo bonds because a formation/deformation of oxo bond significantly changes the Pu–O_{oxo} distances, thereby changing the positions of optical absorption bands. For example, Np(VII) in dilute HClO_4 and that in 2 M H_3PO_4 exhibit significant difference in UV–vis absorption spectra, and the difference is attributed to the change in the number of Np–O oxo bonds.^{8–10}

Pu(VIII) has also been a subject of theoretical study. Straka et al.¹¹ performed B3LYP calculations of Pu(VIII) oxo and

fluoro complexes in the gas phase and concluded that $\text{Pu}^{\text{VIII}}\text{F}_8$ is by far more stable than $\text{Pu}^{\text{VIII}}\text{O}_4$ and, therefore, is the best candidate for synthesizing Pu(VIII) in the gas phase.

In aqueous phase, however, both Pu^{7+} and Pu^{8+} strongly react with solvent water molecules and get stabilized by the formation of Pu–O oxo bonds. Species such as $\text{PuF}_8(\text{aq})$ may only be synthesized under high concentration of fluoride, but such a high fluoride concentration may only be attainable in highly concentrated hydrofluoric acid. Thus far, Pu(VII) is known to exist only in strong alkaline medium.¹

In this work, the redox potential of the Pu(VII)/Pu(VIII) couple in aqueous solution is studied by ab initio quantum chemical calculations, and the feasibility of synthesizing Pu(VIII) in aqueous system is discussed. In recent studies,^{12,13} it has been demonstrated that the quantum chemical calculations can make a reasonable estimate of the redox potentials of the $\text{An}^{\text{V}}\text{O}_2^+/\text{An}^{\text{VI}}\text{O}_2^{2+}$ couples (An = U, Np, Pu, Am) if the spin–orbit effect and the multireference effect are treated properly. The best agreement between the theory and the experiment was obtained for the U(V)/U(VI) couple, the systems with single and no unpaired 5f electron where the multireference effect plays unimportant role. In the redox couple of Pu(VII)/Pu(VIII), the multireference effect can also be neglected and the redox potential can be obtained relatively accurately by the quantum chemical calculations. Since the redox potential of the Pu(VII)/Pu(VIII) couple is experimentally unknown, theoretical calculation can become a powerful tool for estimating the redox potential of the Pu(VII)/Pu(VIII) couple in aqueous solution, thereby giving an answer to the question whether Pu(VIII) is stable in water.

2. Quantum Chemical Calculations

Quantum chemical calculations were performed using Gaussian 03¹⁴ and Molcas 7.0¹⁵ programs. Geometry optimization and vibrational frequency calculations were performed using Gaussian 03 at the B3LYP level in the aqueous phase through the use of conductor-like polarizable continuum model¹⁶ using UAHF radii¹⁷ as implemented in Gaussian 03. Small core

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effective core potentials (ECP) were used on plutonium¹⁸ and oxygen¹⁹ comprising 60 and 2 electrons in the core, respectively, with corresponding basis sets. The most diffuse basis functions on plutonium with the exponent 0.005 were omitted, and a d-function on oxygen basis was included. For hydrogen, a 5s contracted to 3s basis set was used.²⁰ Gibbs energy was calculated as in various recent studies,²¹ through vibrational frequency calculations in the aqueous phase and by using the pressure and temperature parameters $p = 1$ atm and $T = 298.15$ K. All structures were confirmed to be the energy minimum through vibrational frequency analysis with no imaginary vibrational frequency present.

In plutonium complexes, multireference effects originating from strong couplings in the bare ion occur in the systems with more than one unpaired 5f electron.¹² The energies calculated with any unrestricted method are unreliable for strongly multiconfigurational systems. In the present case, Pu(VIII) and Pu(VII) have no and single unpaired 5f electron, respectively, and the multireference effect can hence be neglected. The spin–orbit effect can be neglected for Pu(VIII) because it has a closed-shell electronic configuration, but this effect becomes important for Pu(VII), which has a single unpaired 5f electron. The spin–orbit effect of Pu(VII) species was calculated at the CASSCF level within the variation-perturbation scheme using the RASSI-SO module in Molcas 7.0 program as in a previous study.¹² The spin–orbit calculations were done at the ECP level using the integral mapping procedure.^{15,22} Since the spin–orbit effect is sensitive to degeneracies, the CASSCF calculations were performed without symmetry to avoid artificial symmetry breaking due to the use of only Abelian symmetry groups in the Molcas 7.0 program. The spin–orbit matrix consisted of all states generated by distributing one f-electron in seven f-shells. It was assumed that the spin–orbit effect is additive, and the ground-state energy lowering due to the spin–orbit coupling was added to the spin-free Gibbs energies obtained at the unrestricted B3LYP level.

3. Results and Discussion

3.1. Geometries of Pu(VII) and Pu(VIII) Complexes and Mulliken Population Analysis. Various types of Pu(VII) and Pu(VIII) species with different numbers of Pu–O oxo bonds were computed. The structures and Pu–O_{oxo} bond distances of the calculated complexes are given in Figure 1. The complexes **7a–7i** are those with the oxidation state VII, and **8a1–8i** are those with the oxidation state VIII. The number of oxo bonds was varied from 2 to 5.

The primary interest concerning Pu(VII) and Pu(VIII) speciation is the number of Pu–O oxo bonds, but this is not a question that can be easily answered purely by quantum chemical calculations. Such an attempt was made for Pa(V) by Toraishi et al.,²³ who studied the number of Pa–O oxo bonds in Pa(V) complexes by quantum chemical calculations. Toraishi et al. were led to conclude that the mono-oxo PaO^{3+} is preferred over the dioxo PaO_2^+ because of the 6d (Pa)–2p (O) antibonding orbital formation in the latter complex. However, it should be noted that in aqueous solution a formation/deformation of an oxo bond is a pH-dependent reaction; hence, one cannot necessarily derive a general conclusion as to the question how many oxo bonds are the most stable form. In the Pa(V) case, it is known from an EXAFS study that in 13 M sulfuric acid Pa(V) exists as a mono-oxo complex while in 0.5 M hydrofluoric acid it exists in the absence of any oxo bond.²⁴ Similarly, Np(VII) also takes different numbers of oxo bonds in different medium.^{8–10}

In Figure 1, the coordination number of Pu was varied from 6 to 8. Assuming that both Pu(VII) and Pu(VIII) are only stable

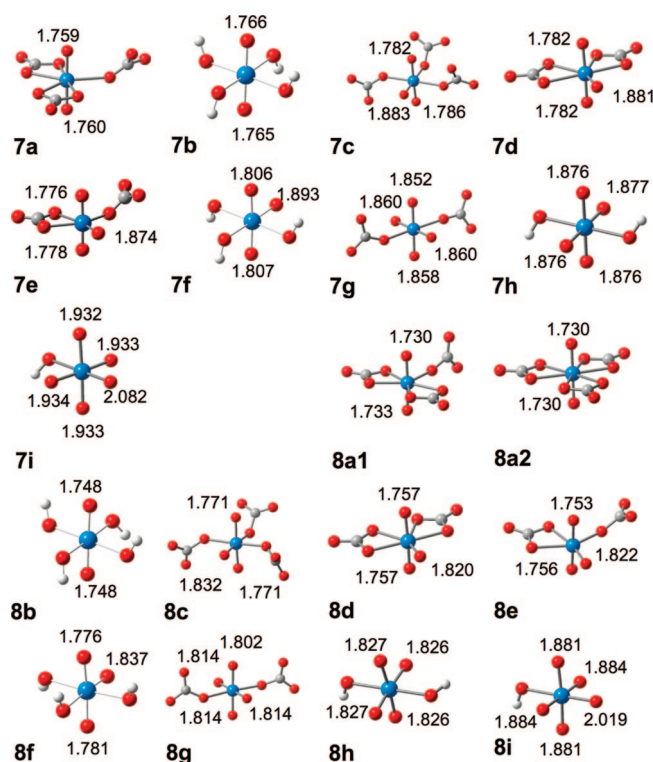


Figure 1. Structures of Pu(VII) (**7a–7i**) and Pu(VIII) (**8a1–8i**) carbonate and hydroxo complexes obtained by B3LYP calculations. The numbers denote the Pu–O oxo bond distances (in angstroms).

TABLE 1: Mulliken Population of Pu(VII) and Pu(VIII) Complexes Obtained at the B3LYP Level

	Pu					O _{oxo} ^a		
	net	breakdown				net	breakdown	
		s	p	d	f		s	p
$\text{PuO}_3(\text{CO}_3)_3^{5-}$ 7c	+1.20	4.25	11.92	11.85	4.69	−0.48	1.84	4.63
$\text{PuO}_3(\text{CO}_3)_3^{4-}$ 8c	+1.14	4.24	11.86	12.02	4.63	−0.35	1.86	4.48
$\text{PuO}_4(\text{CO}_3)_2^{4-}$ 8g	+1.05	4.22	11.86	12.06	4.68	−0.43	1.84	4.58
$\text{PuO}_4(\text{OH})_2^{2-}$ 8h	+1.19	4.18	11.86	12.00	4.65	−0.47	1.83	4.63
$\text{PuO}_5(\text{OH})^{3-}$ 8i	+1.22	4.17	11.89	11.97	4.62	−0.71	1.84	4.87

^a Averaged value.

in strong alkaline solution, all species considered in this study are either hydroxide or carbonate. But later in the discussions, I will come back to this point and discuss whether Pu(VII) and Pu(VIII) are also stable in acidic media. The carbonate binds to Pu in both unidentate and bidentate fashion, but generally prefers the latter. The relative Gibbs energies of unidentate versus bidentate are **8a1** > **8a2**, **8e** > **8d**, and **7e** > **7d**, all preferring the bidentate over the unidentate. When the bidentate coordination is sterically inhibited, the carbonate ligands bind exclusively in unidentate mode (e.g., **7c** and **7g**).

The Pu–O distances are overall shorter in Pu(VIII) complexes compared to that in the corresponding Pu(VII) complexes. To study this point, Mulliken population analysis was performed. Since the absolute value makes little sense in Mulliken population analysis, it was used in a comparative manner by comparing the population of $\text{Pu}^{\text{VII}}\text{O}_3(\text{CO}_3)_3^{5-}$ (**7c** in Figure 1) to that of $\text{Pu}^{\text{VIII}}\text{O}_3(\text{CO}_3)_3^{4-}$ (**8c**). The results are given in the first two lines of Table 1. The plutonium populations are essentially similar in Pu(VII) and Pu(VIII) complexes, and the effective charges of Pu are +1.20 and +1.14, respectively. In Pu(VII) complex, an additional electron (when compared to Pu(VIII)) is localized on oxo and carbonate ligands and the

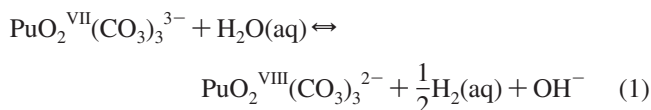
oxygen atoms in Pu(VII) have less covalency compared to those in Pu(VIII). Consequently, the Pu–O oxo bonds get lengthened in Pu(VII) compared to that of the corresponding Pu(VIII) complexes. This situation is in contrast to comparing U(V) versus U(VI) complexes^{12,25} in which an additional electron in U(V) goes mainly into the nonbonding 5f δ and 5f ϕ orbitals and contribute little to the chemical bonding.

When Pu(VII) is oxidized to Pu(VIII), the electron is stripped mainly from the ligand and the plutonium population in Pu(VIII) remains essentially the same as in Pu(VII). Pu(VIII) can be easily reduced back to Pu(VII) through an interaction with surrounding solvent molecules.

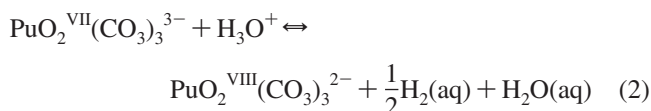
In both Pu(VII) and Pu(VIII) complexes, the Pu–O distances get lengthened as the number of oxo bonds increases. Again, Mulliken population analysis was used to study this point. In Table 1, the Mulliken population of four Pu(VIII) complexes are shown that are PuO₃(CO₃)₃⁴⁻ (Figure 1, **8c**), PuO₄(CO₃)₂⁴⁻ (**8g**), PuO₄(OH)₂²⁻ (**8h**), and PuO₅(OH)₃³⁻ (**8i**). In Pu(VIII) complexes, a significant outflow of electrons from oxygens to plutonium was observed that increased Pu 6d and 5f populations by nearly 2.0 and 4.6 e, respectively. The plutonium population remains essentially similar among all of the four complexes; hence, the effective charge of Pu also remains almost the same value. The deficit of the Pu p population compared to the formal value of 12 suggests that the well-known “6p hole”^{3,26–28} is present here. In contrast to the Pu population, the net charges of oxo oxygens change drastically; they decrease substantially with increasing number of oxo ligands. The oxo oxygens in the complexes with increased number of oxo bonds have less covalency compared to those with fewer number of oxo oxygens. Therefore, the lengthening of the Pu–O oxo bonds in going from trioxo to penta-oxo Pu(VIII) is reflecting the situation that the oxygens are getting more and more ionic as the number of oxo bonds increases.

3.2. Redox Potentials of the Pu(VII)/Pu(VIII) Couples.

The redox potentials of the Pu(VII)/Pu(VIII) couples were calculated from the standard Gibbs energy changes of the redox reactions, ΔG° , as in the previous studies.^{12,13} The reactions are assumed to take place in alkaline solution; hence, OH⁻ was introduced instead of H₃O⁺. For the **7a/8a** redox pair in Figure 1, for example, the reaction to consider is



Since a bare OH⁻ ion is difficult to handle with DFT, it was avoided by combining the following two reactions:



The Gibbs energy change of eq 3 was taken from the experimental value of +79.9 kJ/mol.²⁹

The calculated Gibbs energies include the thermal corrections, the entropy corrections, and also the solvation energy. For Pu(VII) complexes, the ground-state energy lowering due to the spin–orbit effect, which was calculated separately at the CASSCF level, was added to the spin-free Gibbs energies. The spin–orbit effect was first calculated in the absence of the ligand field (OH⁻, CO₃²⁻). The ground-state energy lowering due to the spin–orbit coupling is 58.4, 49.6, 24.1, and 0.3 kJ/mol for PuO₂³⁺, PuO₃⁺, PuO₄⁻, and PuO₅³⁻, respectively. The spin–orbit effect is quite large for PuO₂³⁺ and decreases as the number of oxo ligands increases. According to previous work,^{12,30} the spin–orbit effect in the bare UO₂⁺ ion (which is also an f¹ system) and that in the hydrated one are found to be very similar. In UO₂⁺, the extra electron (compared to the closed-shell U(VI)) goes mainly into the metal atom and makes the ligand field unimportant for the spin–orbit calculation, while in Pu(VII) the extra electron (compared to the closed-shell Pu(VIII)) goes mainly to the ligand and makes it irrelevant to exclude the ligand field in the spin–orbit calculation. Therefore, the spin–orbit effect for Pu(VII) was calculated also in the presence of the ligand field. This was only possible for small clusters, namely PuO₂(OH)₄⁻, PuO₃(OH)₃²⁻, PuO₄(OH)₂³⁻, and PuO₅(OH)₄⁻, in which the ground-state energy lowering due to the spin–orbit coupling was found to be 31.4, 0.3, 4.8, and 6.6 kJ/mol, respectively. The spin–orbit effect drops drastically when the ligands are included in the molecular models. This result is consistent with the previous discussion that in Pu(VII) the electron is localized on the ligand, making the effective charge of Pu in Pu(VII) complex and that in the corresponding Pu(VIII) complexes nearly equal.

For simplicity, the coordination number and the stoichiometry of the complexes were assumed to be equal in all of the redox pairs. The latter assumption may be farfetched as the number of oxo bonds may change upon reduction/oxidation and thereby affect the redox potential significantly. This point will be discussed later in this section.

The redox potentials relative to the standard hydrogen potential of all of the redox couples are given in Table 2. It can be found that the redox potential is largely dependent on the number of the Pu–O oxo bonds; it decreases as the number of oxo ligands increases. The redox potential is insensitive to the type of the coordinating ligand, giving essentially the same number for Pu^{VII}O₄(CO₃)₂⁵⁻/Pu^{VIII}O₄(CO₃)₂⁴⁻ and Pu^{VII}O₄(OH)₂³⁻/Pu^{VIII}O₄(OH)₂²⁻ couples while it is sensitive to the change in the coordination number. From an analogy with Np(VII),⁴ Pu(VII) presumably exist as a tetra-oxo complex in alkaline solution. The redox potential of the tetra-oxo pair, PuO₄(OH)₂³⁻/PuO₄(OH)₂²⁻, is 1.54 V, which is a large value. Pu(VII) and Pu(VIII) may

TABLE 2: Calculated Redox Potentials of Pu(VII)/Pu(VIII) Couples in Alkaline Solution Relative to the Standard Hydrogen Potential and Its Breakdown

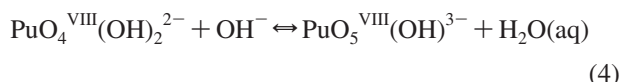
redox pair	7a/8a2^a	7b/8b	7c/8c	7d/8d	7e/8e	7f/8f	7g/8g	7h/8h	7i/8i
oxo bonds	2	2	3	3	3	3	4	4	5
ligand	3 CO ₃ ²⁻	4 OH ⁻	3 CO ₃ ²⁻	2 CO ₃ ²⁻	2 CO ₃ ²⁻	3 OH ⁻	2 CO ₃ ²⁻	2 OH ⁻	1 OH ⁻
ΔG (kJ/mol) ^b	388.8	355.9	233.5	265.5	282.1	238.6	143.5	143.5	95.5
spin–orbit (kJ/mol) ^c	31.4	31.4	0.3	0.3	0.3	0.3	4.8	4.8	6.6
redox potential (V)	4.36	4.01	2.42	2.75	2.93	2.48	1.54	1.54	1.06

^a **8a2** was chosen because its Gibbs energy is 12.4 kJ/mol lower than **8a1**. ^b ΔG of eq 1 without inclusion of the spin–orbit effect. ^c The values for the Pu(VII) hydroxo complexes are given.

possibly take a penta-oxo form in strong alkaline condition by which the redox potential decreases to 1.06 V.

To study the effect of the basis set, the calculation was tested using a better basis set on hydrogen atom; triple- ζ plus polarization function was used.³¹ By improving the hydrogen basis, the redox potential of the $\text{Pu}^{\text{VII}}\text{O}_5\text{OH}^{2-}/\text{Pu}^{\text{VIII}}\text{O}_5\text{OH}^{3-}$ couple changed from 1.06 to 1.09 V. Therefore, I conclude that the choice of the basis set is reasonable considering the aim of the calculations.

A formation/deformation of an oxo bond is a pH-dependent reaction. The reaction to form a penta-oxo Pu(VIII) from a tetra-oxo Pu(VIII) is



The Gibbs energy change of eq 4 obtained at the B3LYP level is +129.7 kJ/mol. It means that the penta-oxo Pu(VIII) is only stable under very high concentration of OH^- . The redox potential of the $\text{Pu}^{\text{VII}}\text{O}_4(\text{OH})_2^{3-}/\text{Pu}^{\text{VIII}}\text{O}_5(\text{OH})^{3-}$ pair is ~ 3 V and is much larger than that of the $\text{Pu}^{\text{VII}}\text{O}_4(\text{OH})_2^{3-}/\text{Pu}^{\text{VIII}}\text{O}_4(\text{OH})_2^{2-}$ pair and the $\text{Pu}^{\text{VII}}\text{O}_5\text{OH}^{2-}/\text{Pu}^{\text{VIII}}\text{O}_5\text{OH}^{3-}$ pair. Therefore, the oxidation of Pu(VII) to Pu(VIII) in alkaline solution is possible only if Pu(VII) exists as a penta-oxo $\text{PuO}_5\text{OH}^{2-}$; otherwise, the redox potential to get Pu(VIII) would be too high.

Thus far, Pu(VII) is known to exist only in alkaline medium. One might speculate that Pu(VII) can also exist in acidic medium because Np(VII) is known to exist also in acidic medium.^{8–10} When the redox reaction takes place in acidic media instead of in alkaline media, the redox potential drops by 0.83 V, which is the Gibbs energy change of eq 3. However, if Pu(VII) exists in acidic medium, it most likely is as a trioxo species because Np(VII) in acidic medium exists as NpO_3^+ . The redox potential of the trioxo Pu(VII)/Pu(VIII) complexes is very high even after subtracting 0.83 V. Hence, Pu(VIII) is unlikely to be obtained under acidic condition.

To summarize, Pu(VIII) may be obtained in strong alkaline solution through an oxidation of Pu(VII), assuming that the starting Pu(VII) species exists as a penta-oxo complex. Therefore, to study the feasibility to get Pu(VIII) in aqueous solution, it is mandatory to first characterize the structures of Pu(VII) complexes in a wide range of pH and in the presence of various types of ligands. Such a study using extended X-ray absorption fine structure spectroscopy is ongoing for Np(VII)³² and may be extended in the future to Pu(VII). However, when Pu(VII) is oxidized to Pu(VIII), the electron is deprived mainly from the ligand and not from the central metal. Hence, Pu(VIII) is most likely to be reduced back to Pu(VII) by the surrounding solvent molecules rather quickly. It is unclear how accurate the present model is to reproduce the redox potential in strong alkaline solution where the activity of water is low and conventional polarized continuum model can poorly describe the solvation shells. New types of approaches, such as that of Martin et al.,³³ might be necessary to investigate this type of system. It is also worthwhile to study if Pu(VIII) is stable in nonaqueous solvent, which has a large redox window. These points need further investigation.

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Supporting Information Available: Coordinates and Gibbs energies of all complexes in Figure 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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