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## A semiempirical approach toward the origin of *f*-element binding selectivity of pyridine-2,6-diylbis(diphenylphosphine oxide)

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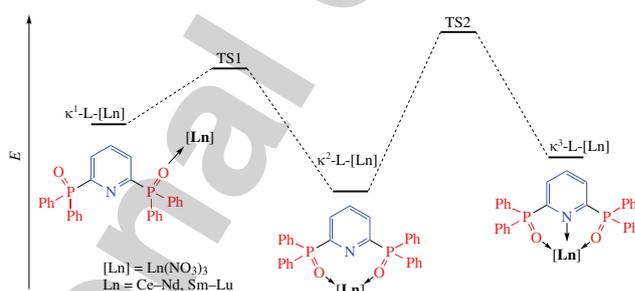
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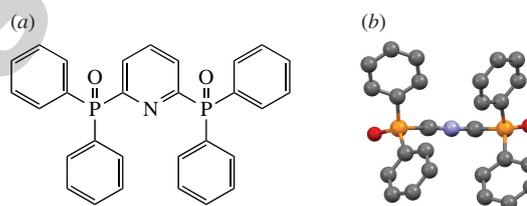
The geometries of a series of lanthanide complexes with phosphine oxide-type ligands (either mono- or polydentate) were optimized using the PM6/Sparkle semiempirical computational approach. The activation barriers of coordination reactions (*i.e.* the conversion of a complex with  $\kappa^1$ -bound ligand into a complex with multiply bound one) were estimated. The  $\kappa^2$ -chelate formation with a pyridine-2,6-diylbis(diphenylphosphine oxide) ligand is favorable only for a few largest lanthanides, while  $\kappa^1$ -coordination is the most probable case for the smaller ones.



**Keywords:** phosphine oxide, lanthanides, PM6, Sparkle, complexation.

The most important application of tertiary phosphine oxides is the synthesis of coordination compounds with *s*,<sup>1,2</sup> *p*,<sup>3,4</sup> *d*<sup>5–7</sup> and *f* metals.<sup>8,9</sup> The phosphine oxide complexes of *4f* elements possess useful physicochemical properties,<sup>10,11</sup> and they are of great significance in the separation of lanthanides and actinides within a nuclear fuel reprocessing cycle.<sup>12,13</sup> This separation is very difficult and laborious because of similar electronic structures and chemical behaviors of *f* elements, and it can be performed by liquid–liquid extraction with complexation agents containing donor groups such as carbonyl (in amides), phosphine chalcogenide (in oxides, sulfides, oxo and thio acids), and N-heterocycle, which provide high distribution coefficients (*D*) and separation factors (SF).<sup>13</sup> Recently, a simple phosphine oxide-type extractant, pyridine-2,6-diylbis(diphenylphosphine oxide) **1** [Figure 1(a)], was found to have significant selectivity for Am/Cm and Am/Eu,<sup>14</sup> and slight bond length differences found in DFT-optimized structures were proposed as a reason for the selectivity. We conducted the modeling of the complexation of ligand **1** and several metal ions to understand the origin of selectivity and the coordinating ability of the ligand. Since DFT calculations for *f*-element compounds are expensive in terms of hardware resources, the Sparkle/PM6<sup>15</sup> level of theory (in the MOPAC2016<sup>16</sup> computational package with the Galedit<sup>17</sup> software as a graphical interface) was used for the optimization of geometries of lanthanide complexes.<sup>†</sup>

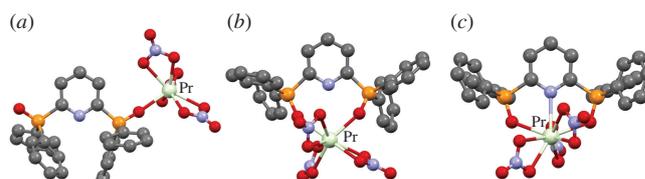
The first step was ligand geometry optimization by the use of a PM6 semiempirical method. All four phenyl substituents were directed toward each other, and two oxygen atoms of phosphine oxide moieties were pointed away from the pyridine ring and P–O bonds located nearly in its plane [Figure 1(b)]. The same conformation was previously found in solid state using X-ray



**Figure 1** (a) Chemical structure and (b) PM6-optimized conformation of compound **1**.

crystallography.<sup>19</sup> In principle, a polydentate ligand, having an appropriate geometry, can act as a chelating one when the pathway is energetically favorable, or it can bridge two metal centers when chelation creates significant strain in the ligand backbone. Calculations revealed that the ligand's lowest energy conformation is unsuitable for chelate formation as all three donor atoms are oriented in different directions, and we assumed that the conformation is preserved in solution.

Further, it is more likely that the first complexation event would be with phosphine oxide oxygen rather than heterocyclic nitrogen since bulky phenyl groups shield the latter from the environment. Regardless of the complex formed, either a chelate or a polymer, the starting material for both would be the same and had the ligand attached to a metal center by one of the phosphine oxide oxygens – an ‘open’ complex ( $\kappa^1$ -**1**-M) [Figure 2(a)]. After overcoming an activation barrier, complex



**Figure 2** Complexes (a)  $\kappa^1$ -**1**-Pr, (b)  $\kappa^2$ -**1**-Pr and (c)  $\kappa^3$ -**1**-Pr of Pr(NO<sub>3</sub>)<sub>3</sub> with **1**.

<sup>†</sup> Although a newer version of the parametrization is available,<sup>18</sup> it was pointed out that the presence of phosphorus atoms in complexes caused large errors in the resulting geometries.

**Table 1** Enthalpy parameters (kcal mol<sup>-1</sup>) for lanthanide complexes with **1**.

Entry		Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1 <sup>a</sup>	<b>1</b> + M(NO <sub>3</sub> ) <sub>3</sub>	47.51	56.90	48.55	55.06	46.48	51.66	43.31	64.73	56.46	41.52	46.77	53.23	53.13
2	$\kappa^1$ - <b>1</b> -M	0	0	0	0	0	0	0	0	0	0	0	0	0
3	TS1	2.86	5.24	5.63	3.92	37.79	1.79	27.50	39.85	7.47	13.91	25.84	20.84	23.47
4	$\kappa^2$ - <b>1</b> -M	-30.45	-28.63	-34.51	-30.44	-16.97	-27.08	-18.68	-26.24	-25.18	-16.20	-21.87	-20.05	-19.68
5 <sup>b</sup>	TS2	-25.86	-25.18	-15.58	-22.42	19.09	15.83	14.58	16.70	-12.79	7.60	9.64	1.17	5.72
		<u>4.58</u>	<u>3.45</u>	<u>18.93</u>	<u>8.02</u>	<u>36.06</u>	<u>11.2</u>	<u>33.26</u>	<u>42.94</u>	<u>12.39</u>	<u>23.80</u>	<u>31.51</u>	<u>21.22</u>	<u>25.40</u>
6	$\kappa^3$ - <b>1</b> -M	-37.45	-30.74	-38.59	-29.63	-0.57	-22.26	-1.48	-15.00	-21.33	-10.30	-6.33	-10.61	-4.55
7 <sup>a</sup>	$\kappa^1$ - <b>1</b> -M + <b>1</b>	0	0	0	0	0	0	0	0	0	0	0	0	0
8	( $\kappa^1$ - <b>1</b> ) <sub>2</sub> -M	-47.10	-48.18	-46.36	-47.56	-36.00	-43.76	-36.07	-21.27	-45.31	-32.38	-39.03	-40.83	-41.42

<sup>a</sup>The values are calculated for two fragments at an infinite distance. <sup>b</sup>The underlined values are the barrier heights relative to the values in entry 4.

$\kappa^1$ -**1**-M turns into a chelate ( $\kappa^2$ -**1**-M or  $\kappa^3$ -**1**-M) [Figures 2(b),(c)].

To probe the feasibility of the chelate formation, we optimized the geometries of complexes  $\kappa^1$ -**1**-M of lanthanides from Ce to Lu with the exception of Pm at the Sparkle/PM6 level of theory (Table 1, entry 2). Then, we brought a lanthanide atom and the non-coordinated phosphine oxide oxygen atom in **1** together at a rate of 0.01 Å per step with system geometry optimization in each step. The result of these calculations was a series of potential energy curves with the highest-energy point corresponding to the transition state (Table 1, entry 3) and the lowest-energy one corresponding to a chelate complex (entry 4). Note that no coordination was found between a lanthanide atom and the heterocyclic nitrogen in any of the complexes. Once again, a lanthanide and this heterocyclic nitrogen were moved towards each other and potential energy curves were obtained for all metals, including corresponding TS2 (Table 1, entry 5) and products  $\kappa^3$ -**1**-M (entry 6). First, there is the following trend in TS1 values: for largest lanthanides, cerium and praseodymium, these values are very low, for two next lanthanides, neodymium and samarium, they are slightly larger, while these parameters for other lanthanides are significantly larger. Two exceptions, gadolinium and holmium, can be explained by computational model imperfection since they should have similar chemical properties with their neighbors. Qualitatively, these results can be interpreted in the following way: larger cations connect two oxygens more easily and with less distortions in the ligand backbone. The formation of complexes  $\kappa^2$ -**1**-M in all cases was calculated to be exergonic (Table 1, entry 4) with a slight decrease of the effect along the lanthanide series.

Then, the modeling of M–N bonding in complexes  $\kappa^2$ -**1**-M leading to complexes  $\kappa^3$ -**1**-M was conducted. This ‘reaction’ for two largest lanthanides proceeds with lowest barriers in series (TS2), while significantly larger activation barriers were estimated for other lanthanides; these values are also higher than the barriers of chelation (TS1). It is reasonable because greater distortions of the ligand structure are expected when shorter M–N bonds are formed. More importantly, in all cases except the first three ones, the formation of  $\kappa^3$ -chelates was assessed to be endergonic; note that minimum-energy geometries for Ce, Pr and Nd compounds contain metal atoms outside the pyridine ring plane, while a metal atom is located directly in that plane for heavier congeners. It means that the formation of  $\kappa^2$ -chelates is preferred for ligand **1** and lanthanides over  $\kappa^3$ -analogues.

The enthalpy of formation of complexes  $\kappa^1$ -**1**-M was also estimated. All values are negative and close to each other; they fall in a range of 40–60 kcal mol<sup>-1</sup> (Table 1, entry 1). These values are significantly higher than enthalpies of chelation (16–35 kcal mol<sup>-1</sup>); moreover, first complexations were calculated to be essentially barrierless. These results led us to the assumption that the addition of another molecule of **1** to

complexes  $\kappa^1$ -**1**-M can take place instead of chelation leading to  $\kappa^2$ -**1**-M or  $\kappa^3$ -**1**-M. For all lanthanides, this reaction was found to be enthalpically favorable with 20–50 kcal mol<sup>-1</sup> (Table 1, entry 8). Thus, it seems reasonable to conclude that the formation of complexes ( $\kappa^1$ -**1**)<sub>2</sub>-M can be preferred over chelating  $\kappa^2$ -**1**-M or  $\kappa^3$ -**1**-M.

To obtain experimental evidence on the structure of lanthanide complexes with **1**, we tried to grow X-ray quality crystals from the mixtures consisting of a metal nitrate and **1**, but our attempts were unsuccessful. However, there is an example of a coordination polymer obtained from **1** and Pr(NO<sub>3</sub>)<sub>3</sub>.<sup>20</sup> The polymer formation, obviously, does not prove our hypothesis, but it at least does not contradict it. It is well known that tin(IV) formed<sup>21</sup> a chelating complex [( $\kappa^3$ -**1**)SnCl<sub>3</sub>]<sup>+</sup>[SbCl<sub>6</sub>]<sup>-</sup> with **1**; thus, it seems reasonable to estimate computationally the activation barrier of the chelation reaction, which was found essentially zero at the PM6 level of theory. The calculated enthalpy was -25.69 kcal mol<sup>-1</sup>. The result demonstrates that the chelation of tin is significantly more feasible than that of early 4f elements, not to mention heavier ones. Since the tin atom is much smaller than lanthanides, it should be easier for it to enter the ligand cavity with bonding with all three donor atoms.

Another example of lanthanide complexes with diphosphine dioxide-type ligand is ethane-1,2-diylbis(diphenylphosphine oxide) (dppeO<sub>2</sub>) **2**.<sup>22</sup> The ethylene linkage of this ligand is much more flexible than a rigid aromatic pyridyl fragment in pyridine-2,6-diylbis(diphenylphosphine oxide); thus, it is reasonable to anticipate that the former ligand would form chelates more readily than the latter. Indeed, chelate formation was observed for Pr and Lu.<sup>22</sup> PM6/Sparkle calculations were conducted to investigate chelation barrier heights, and the results are summarized in Table 2. As before, the formation of chelates is exothermic, but activation barriers in this case are significantly lower than those with **1**. Furthermore, although Spichal *et al.*<sup>22</sup> aimed at polymeric materials synthesis, they were unable to obtain any polymer starting from Lu(NO<sub>3</sub>)<sub>3</sub> and **2**, which is in qualitative agreement with a small activation energy calculated for the formation of  $\kappa^2$ -**2**-Lu.

Let us return to the selectivity of compound **1** for Am/Eu and Am/Cm separations.<sup>14</sup> Note that we did not conduct any calculations for the actinide family since there is no reliable parametrization available, but further discussion will be based on the assumption that trends in ionic sizes and binding modes with

**Table 2** Calculated parameters (kcal mol<sup>-1</sup>) for lanthanide (Sparkle/PM6) complexes with **2**.

	Pr	Lu
$\kappa^1$ - <b>2</b> -M	0	0
TS	–	15.23
$\kappa^2$ - <b>2</b> -M	-35.58	-29.41

phosphine oxide groups are similar for 4*f* and 5*f* elements. Three main points can be deduced from our computational results: (1) the formation of complexes  $\kappa^2\text{-2-M}$  is both kinetically and thermodynamically feasible for all the lanthanides; (2) complexes  $\kappa^3\text{-2-M}$  are higher in energy than corresponding analogues  $\kappa^2\text{-2-M}$  for all except first three metals; in addition, activation barriers are larger than in chelation; (3) the coordination of another molecule of **1** to a  $\kappa^1\text{-1-M}$  with the generation of complex  $(\kappa^1\text{-1})_2\text{-M}$  is at least as probable as a pathway towards  $\kappa^2\text{-2-M}$ . Combining the statements, we can conclude that **1** can act as a chelating ligand for bigger ions, while it is necessary to take into account the formation of complexes  $\kappa^1\text{-1-M}$  and  $(\kappa^1\text{-1})_2\text{-M}$  (and, probably, polymeric ones) for smaller ones when discussing the binding selectivity. In a set of three *f* elements (Am, Cm, and Eu), the size of ions decreased in the given order. If our anticipation is reasonable, it can be expected that **1** should bind with Am preferentially and differences in binding efficiency should be more remarkable for the Am/Eu pair than for Am/Cm. Matveev *et al.*<sup>14</sup> found that, under their conditions, the selectivity factors were about 8 and about 3 for the former and the latter pairs, respectively. These values are in excellent agreement with our hypothesis, supporting that the  $\kappa^2$ -chelate formation is the origin of the observable differences. The other mode of reactivity of **1** may be expected from the results obtained for a Sn complex. In this case (and, probably, in the cases of other ions of comparable sizes),  $\kappa^3$ -complex is the most stable form of the coordination of **1**, and this fact can be used for ion separation with larger factors.

In conclusion, by the modeling of a reaction between lanthanide ions and phosphine oxide-type ligands **1** and **2**, we have shown that the PM6/Sparkle computational method is reliable not only for the geometry optimization of lanthanide compounds but also for the qualitative estimation of activation barriers. The origin of the binding selectivity of **1** in the Am–Cm–Eu series was anticipated to be the result of easier  $\kappa^2$ -chelate formation in cases of larger ions, which is in good agreement with the experimental data. The ease of the formation of chelate complexes is governed by the size of the ions.

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#### Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.09.011.

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