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Regular article

Ab initio calculations with effective core potentials on trivalent lanthanide–terpyridine complexes

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Abstract. The electronic structures of complexes of terpyridine (tpy) with trivalent lanthanides (Ln) were calculated using ab initio methods with effective core potentials at Hartree–Fock and post-Hartree–Fock levels of theory. The quasirelativistic large-core (with 4*f* electrons included in the core) pseudopotentials of the Stuttgart group were chosen for the Ln atoms. The variation of several properties of the Ln(tpy)³⁺ complexes was studied for the whole Ln series. It was shown that there was a monotonous variation for all properties (geometrical and energetic) along the Ln series, except for Mulliken charges on the metal atom. Calculations were performed on three complexes of known solid-state structure. The difference between experimental and calculated geometries is discussed; for all structures, it is found to be lower than 0.2 Å. In all cases, the relative order from one complex to another is conserved.

Key words: Pseudopotentials – Lanthanides complexes

based on the use of theoretical chemistry (molecular dynamics simulations and quantum chemistry) in order to achieve the previously defined goals. In this frame, quantum chemistry could be used as a tool to better understand the differences in An and Ln reactivity with N-bearing ligands.

Effective core potential (ECP), or pseudopotential, methods were chosen to study the electronic structure of Ln and An complexes. This choice was dictated by the need to compare An and Ln and to study systems of large size (more than 30 atoms). The present article reports, as a first step in our progressive methodology, the investigation of the reliability of such methods to determine geometries and energies of Ln complexes with N-donor ligands. 2,2′:6′:2″-Terpyridine (tpy, Fig. 1) was chosen as a representative element of these ligands. The effect of the pseudopotential type on the calculation results was studied. Then, with the selected method, the whole series of [Ln(tpy)]³⁺ complexes was analyzed. The variation of several parameters along the series and according to the level of theory is discussed. Finally, the calculated geometry of [Ln(tpy)(H₂O)_{*n*}Cl]²⁺ is compared to experimental data.

1 Introduction

In the field of nuclear fuels reprocessing special emphasis is put on the separation of the minor actinides (An), i.e. neptunium, americium, and curium from the other elements present in spent fuels [1, 2]. This is not a simple task to achieve, particularly for Am(III) and Cm(III) the chemical properties of which are very similar to those of the trivalent lanthanides (Ln(III)), which are also present in nuclear waste, and which account for about one-third of the total fission products inventory. The An(III)/Ln(III) group separation may be achieved by liquid–liquid extraction systems involving soft-donor extractants [3]. The investigation of factors affecting the stability of the complexes and the understanding of metal–ligand interaction is, though, of great importance in the design of new ligands. Our general methodology is

2 Computational details

Ab initio calculations were made at the Hartree–Fock (HF) or at the second order Møller–Plesset perturbation (MP2) level of theory with Gaussian 94 [4] and Gaussian 98 [5] programs using SGI workstations. Full geometry optimization of all molecular systems was carried out without symmetry constraints. Considering the chemical hypothesis that 4*f* orbitals of Ln cations do not contribute much to the reactivity of these elements and in order to reduce computational time, the choice of large-core pseudopotentials was made. Several pseudopotentials were used for the calculations of [La(tpy)]³⁺ complexes: both nonrelativistic and quasirelativistic energy-adjusted ECPs of Dolg and coworkers [6] and the quasirelativistic ECPs of Hay and Wadt [7], Ross et al. [8], and Stevens et al. [9] adjusted on orbitals. All other Ln compounds were calculated using quasi-

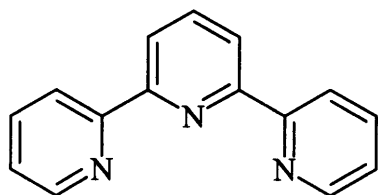


Fig. 1. 2,2':6':2''-Terpyridine (*tpy*) ligand. Representation of its complexing conformation

relativistic Dolg pseudopotentials for Ln atoms, where $46 + 4f^n$ electrons are included in the core and the Ln are modeled as 11-valence-electron systems. The contracted $(7s6p5d)/[5s4p3d]$ Gaussian-type orbital valence basis sets were used for the Ln and the polarized all-electron 6-31G(d) basis sets for all other atoms. The basis set superposition error (BSSE) was calculated for two tpy complexes of Ln ($[\text{La}(\text{tpy})]^{3+}$ and $[\text{Lu}(\text{tpy})]^{3+}$) using the counterpoise method [10]. It was found to be small (1.2 and 1.1% of the interaction energy for La and Lu complexes, respectively), so the interaction energies obtained in the following calculations are without BSSE correction.

3 Results and discussion

3.1 Influence of ECPs and relativistic effects

The study of the influence of pseudopotential type was made on the $[\text{La}(\text{tpy})]^{3+}$ complex using four different large-core ECPs [6–9]. Since the results (geometries and La–ligand interaction energies) obtained with the different pseudopotentials are very similar (Table 1), the choice of the energy-adjusted ECPs of Dolg and coworkers [6] was made according to the following practical considerations: pseudopotentials are available for the whole Ln series and pseudopotentials developed with the same scheme are also available for the Ar elements. The geometries of the $[\text{La}(\text{tpy})]^{3+}$ and $[\text{Lu}(\text{tpy})]^{3+}$ complexes were fully optimized using the nonrelativistic and quasirelativistic pseudopotentials of Dolg and coworkers [6]. As shown in Table 2, the relativistic effects do influence the structures of the complexes. The use of quasirelativistic pseudopotentials induces an increasing bond length contraction from La to Lu, since Lu exhibits larger relativistic effects than La.

Table 1. Lanthanum Mulliken atomic charge, La–N distances (Å), and La–ligand interaction energy [calculated as $E_{\text{complex}} - (E_{\text{tpy}} + E_{\text{La}^{3+}})$] for $[\text{La}(\text{terpyridine})]^{3+}$ complexes (Hartree–Fock, HF calculations). Influence of the pseudopotential

	Dolg and coworkers[6]	Hay and Wadt[7]	Ross et al.[8]	Stevens et al.[9]
q_{La}	+2.46	+2.29	+2.38	+2.39
La–N _{central} (Å)	2.49	2.49	2.49	2.49
La–N _{lateral} (Å)	2.47	2.47	2.47	2.48
$E_{\text{int.}}$ (kcal/mol)	–325.3	–327.6	–327.1	–325.4

Table 2. Lanthanide (Ln)–N distances in the $[\text{La}(\text{tpy})]^{3+}$ and $[\text{Lu}(\text{tpy})]^{3+}$ complexes (calculated at the HF level of theory). Influence of the relativistic effects

	Nonrelativistic		Quasirelativistic	
	Ln–N _{central} (Å)	Ln–N _{lateral} (Å)	Ln–N _{central} (Å)	Ln–N _{lateral} (Å)
$[\text{La}(\text{tpy})]^{3+}$	2.51	2.48	2.49	2.47
$[\text{Lu}(\text{tpy})]^{3+}$	2.28	2.32	2.23	2.29

This result confirms that relativistic effects are not negligible for Ln elements and that they should be taken into account in the calculations.

3.2 Study of $[\text{Ln}(\text{tpy})]^{3+}$ complexes

The electronic structures of 1:1 $[\text{Ln}(\text{tpy})]^{3+}$ complexes were calculated at the HF level for Ln = La – Lu and at the MP2 level for Ln = La, Eu, and Lu to investigate the effect of electron correlation. All calculated complexes have planar geometries, where the cation is bonded to the ligand in a symmetric way in the area between the three binding N atoms. Variations of Ln–N bond lengths at the equilibrium geometry determined at the HF and MP2 levels are shown in Fig. 2. The Ln–N bond lengths decrease monotonously with the increase in the atomic number of Ln according to the Ln contraction (decrease in Ln ionic radii along the series). The MP2 geometries are very close to the HF ones. The electron correlation has almost no effect on the Ln–N_{central} bond lengths, while the Ln–N_{lateral} ones decrease by 0.01–0.02 Å. Note that the bond distance between Ln and the central N atom of the ligand decreases more sharply than that with the lateral N atoms. The Ln atom, while decreasing in size, comes closer to the central nitrogen than to the lateral nitrogens. This is due to the steric constraints of the ligand, since the distance between the two lateral nitrogens remains almost constant for all complexes. This was observed in experimental solid-state structures of $[\text{Ln}(\text{tpy})(\text{H}_2\text{O})_n\text{Cl}]^{2+}$ (n varying from 5 to 4 along the

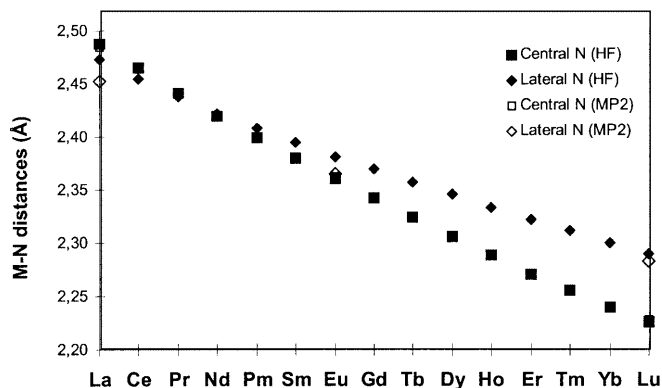


Fig. 2. Variation of lanthanide (Ln)–N bond distances (Å) along the Ln series for $[\text{Ln}(\text{tpy})]^{3+}$ 1:1 complexes

Ln series) complexes [11] where the Ln–N_{central} bond length varies from 2.69 to 2.44 Å, while the Ln–N_{lateral} bond length varies from 2.66 to 2.46 Å.

Figure 3 shows that the Mulliken net charge of Ln decreases from +2.46 to +2.40 with increasing atomic number. The covalent character of the Ln–N bond, which can be estimated from the deviation of the Ln net charges from +3, increases slightly along the series. Note that the deviation of the Ln net charge from the straight line observed for Pm, Sm, Gd, and Lu complexes does not seem to have any physical origin and may arise from the convergence criterion that was used. The observation of such deviation was already made by Tsuchiya et al. [12] concerning the net charge of Sm in the series of LnCl₃ complexes calculated by pseudopotential methods at the complete-active-space self-consistent-field level. Note finally that, at the MP2 level, the same dependence on the atomic number as at the HF level is observed, but the absolute values are 0.26–0.28e smaller.

The metal–ligand interaction energy calculated as $E_{\text{complex}} - (E_{\text{tpy}} + E_{\text{Ln}^{3+}})$ for all complexes along the Ln series is shown in Fig. 4. This energy decreases (becomes more negative) with increasing atomic number. Indeed, due to the Ln contraction, the Ln atom comes closer to the ligand, inducing stronger interaction (attraction) between both entities. Interaction energies calculated at the MP2 level are slightly more negative. Lanza and

Fragalà [13] observed comparable results for CeX₃ complexes calculated with the pseudopotentials of Stevens et al. [9] and a [4*s*,2*d*,2*f*] contracted basis set for Ce and a 6-31G(d) basis-set for Cl. For those compounds, the comparison with experimental data showed that the interaction energy, ΔE , calculated at the HF level is slightly underestimated due to the lack of correlation effects, while ΔE calculated at the MP2 level is overestimated; however, both ΔE are very similar. Our results for tpy complexes are in line with those observations despite the lack of thermodynamic experimental data for comparison.

3.3 Calculation of $[\text{Ln}(\text{tpy})(\text{H}_2\text{O})_n\text{Cl}]^{2+}$ complexes of known experimental structure

Three complexes of known solid-state structure [11], $[\text{La}(\text{tpy})(\text{H}_2\text{O})_5\text{Cl}]^{2+}$, $[\text{Eu}(\text{tpy})(\text{H}_2\text{O})_5\text{Cl}]^{2+}$, and $[\text{Lu}(\text{tpy})(\text{H}_2\text{O})_4\text{Cl}]^{2+}$, were fully optimized at the HF level of theory starting from the experimental structures. These calculations aimed to compare experimental and calculated geometry. Considering that the calculations were made for the gas phase and that the experimental data refer to the solid phase, the calculated geometries do not differ much from the experimental ones. The general coordination pattern is the same for experimental and calculated complexes (Fig. 5). Some deviation is observed for water ligands; however, it may not be reasonable to compare the exact locations of the water ligands because they are strongly dependent on the crystal packing and on the structure of the second coordination sphere. A more precise comparison of Ln–ligand bond lengths is made in Table 3. Note that the calculation systematically overestimates the Ln–ligand bond lengths. The largest difference is observed for Ln–O bonds with the water molecules ($\Delta l \sim 0.17\text{\AA}$). Note also that the Ln–N (with tpy ligand) and the Ln–O (with water) bond lengths have very similar calculated values, whereas the experimental values differ

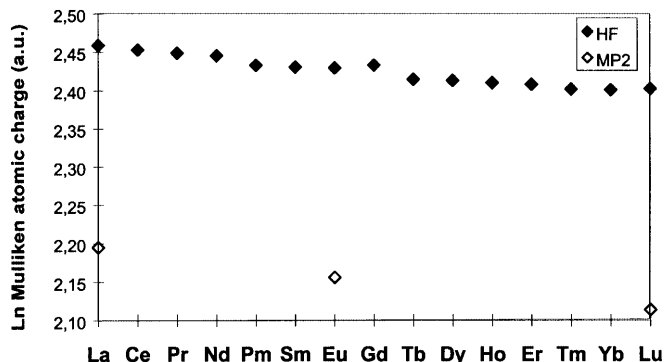


Fig. 3. $[\text{Ln}(\text{tpy})]^{3+}$ 1:1 complexes. Variation of Mulliken Ln atomic charge (au) along the Ln series

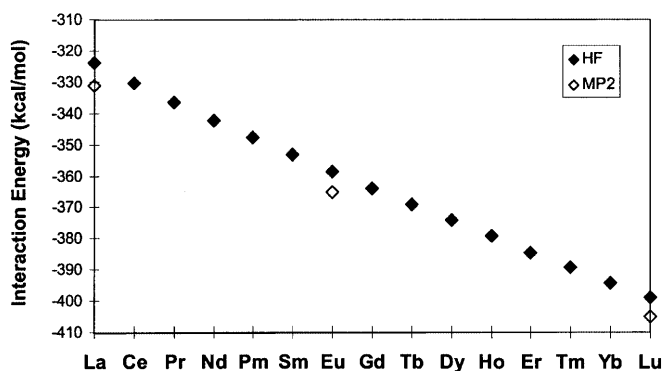


Fig. 4. $[\text{Ln}(\text{tpy})]^{3+}$ 1:1 complexes. Variation of metal–ligand interaction energy (kcal/mol) along the Ln series

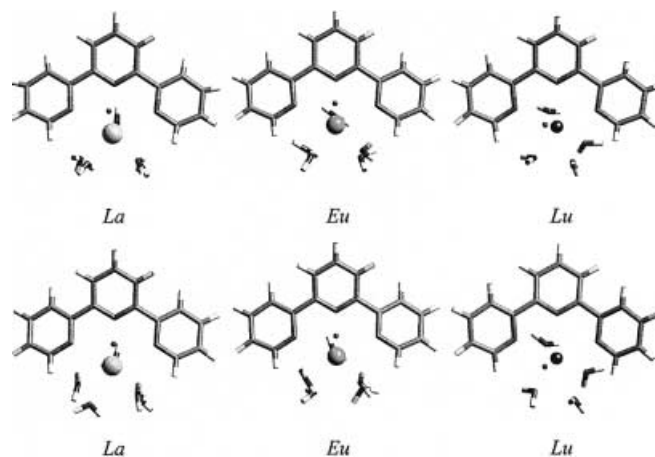


Fig. 5. $[\text{La}(\text{tpy})(\text{H}_2\text{O})_5\text{Cl}]^{2+}$, $[\text{Eu}(\text{tpy})(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ and $[\text{Lu}(\text{tpy})(\text{H}_2\text{O})_4\text{Cl}]^{2+}$ complexes. Experimental (top) and calculated (bottom) structures. C: grey, O: red, N: blue, H: white, Cl: dark green, La: yellow, Eu: light green, Lu: purple

Table 3. Mean lengths (Å) of metal–ligand donor atom bonds for [La(tpy)(H₂O)₅-Cl]²⁺, [Eu(tpy)(H₂O)₅Cl]²⁺, and [Lu(tpy)(H₂O)₄Cl]²⁺ complexes. Comparison between calculated and experimental structures

Bond (Å)	Experimental [6]			Calculated (HF)			Difference		
	La	Eu	Lu	La	Eu	Lu	La	Eu	Lu
Ln–N _{central}	2.69	2.54	2.44	2.73	2.61	2.46	0.04	0.07	0.02
Ln–N _{lateral}	2.66	2.55	2.46	2.72	2.62	2.50	0.06	0.07	0.04
Ln–O _{water}	2.56	2.48	2.31	2.72	2.63	2.50	0.16	0.15	0.19
Ln–Cl	2.90	2.75	2.65	2.82	2.72	2.56	0.08	0.03	0.09

by approximately 0.1 Å. This could be due to the 6-31G(d) basis set used for O and N atoms which does not differentiate these atoms sufficiently.

4 Conclusion

The electronic and geometrical structures of complexes of the series of Ln with tpy ligand was investigated. The validity of ab initio quantum chemistry calculations with quasirelativistic large-core pseudopotentials for large complexes of *f* elements (restricted to 1:*n* complexes with one *f* element) was demonstrated.

It was shown that there was a regular variation of geometrical and energetic parameters along the Ln series for [Ln(tpy)]³⁺ complexes, which is in line with the chemical knowledge of such compounds. The effect of electron correlation was not found to be very important in these complexes.

The comparison with experimental geometries, for three complexes of the [Ln(tpy)(H₂O)_{*n*}Cl]²⁺ series, showed systematically slightly longer calculated bond lengths. The deviations may be due to the effect of crystal packing forces in the solid, which induce shorter Ln–ligand distances than those calculated in the gas phase. Furthermore, calculations taking better into account the electron correlation could also result in shorter bond lengths, as shown in the MP2 calculations of [Ln(tpy)]³⁺ complexes even if this shortening is not sufficient.

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