Structure and separation quality of various N- and O-donor ligands from quantum-chemical calculations

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Abstract. Although BTP (2,6-di(1,2,4-triazin-3-yl)pyridine) has been proven to be a highly effective N-donor ligand for the selective An(III)/Ln(III) separation, the origin of its selectivity is still under discussion. We present in this paper quantum-chemical calculations at the density functional theory (DFT) and MP2 level which highlight the role of the aquo ions in the separation process. Furthermore these data will be the reference for future force-field development to investigate the differences in An(III) complexation reactions compared to their Ln(III) counterparts.

Key words: actinide chemistry • extracting ligands • lanthanide chemistry • quantum chemistry • separation factor

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Introduction

The study of the behavior of actinide and lanthanide ions in aqueous solution and their differences plays a major role in understanding separation processes as applied in the partitioning and transmutation (P&T) approach. Many studies have shown that high separation factors can be achieved by certain soft N-donor ligands based on the BTP and BTBP type (see [1] and references therein). Despite that effort there are still ongoing debates why structurally similar ligands do not work as well or even fail already to form a stable complex. Considerable progress has been made, however, in understanding particular parts of the ligands' properties like structure, solubility and solvent influence studied by a variety of setups including nuclear magnetic resonance (NMR), time-resolved laser fluorescence spectroscopy (TRLFS), UV-Vis and extended X-ray absorption fine structure (EXAFS) [1–5]. Also theoretical studies tried to shed light into the complex actinide-nitrogen bond [6–13], but due to the large system size one is often restricted to DFT or simplified model systems treating the aromatic rings separately. Description of the solvent in quantum-chemical (QM) calculations is rather demanding as it introduces many new degrees of freedom and adds even more to the number of explicitly treated atoms, whereas results using polarizable continuum models to mimic the solvent have to be treated with care when the cavity is too close to the highly charged metal ions. To overcome these limitations we are developing accurate force

fields adjusted to *ab initio* calculations which later will be used to perform molecular dynamics simulations. As a starting point for the QM reference points structure optimizations are performed. In this paper we will present results on the structure and binding energies obtained for various Cm(III)/Gd(III) 1:2 and 1:3 complexes with N-donor, O-donor and mixed N/O-donor ligands.

Quantum-chemical methods

For both ions Cm(III) and Gd(III), which are relevant representatives for separation qualities of extracting ligands, the structure of the 1:2 complex (for 4-dentate ligands) or 1:3 complex (for 3-dentate ligands) was optimized employing density functional theory (DFT) using the BH-LYP functional [14] with an m5 grid as implemented in the TURBOMOLE software package [15]. The BH-LYP functional was chosen for its better convergence compared to other hybrid-functionals while providing similar structural results. Basis sets of triple zeta quality have been used on all ligands and the small-core relativistic pseudopotentials (Cm/ECP60MWB and Gd/ECP28MWB) with corresponding basis sets on the metal ions [16]. In all systems we use the high-spin $^8S_{7/2}$ state.

In a second step, the interaction energy E_g corrected for basis-set superposition error is computed on the MP2 level employing the resolution of the identity technique [17, 18]. Here we use the counter-poise method considering the metal ion and the total ligand structure as fragments [19].

$$(1) \qquad E_g(ML_3) = E(ML_3) - E(M)^{+L_3 \text{basis-functions}}$$
$$- E(L_3)^{+M \text{basis-functions}}$$

An estimate for the reaction Gibbs-free energy in solution G_{aq} is obtained by adding the solvation energy G_{sol} from a single-point calculation using a continuum model (COSMO [20]) based on the optimized gas-phase structures. As suggested by Ho *et al.* [21], we derive G_{sol} on the Hartree-Fock level. The COSMO cavity is constructed using the default radii $r_o = 1.72$ Å, $r_p = 2.11$ Å, $r_s = 2.16$ Å, $r_H = 1.30$ Å, $r_C = 2.00$ Å, $r_N = 1.38$ Å and for the metal ions $r_{Cm} = 1.72$ Å and $r_{Gd} = 1.72$ Å. As already pointed out by Bryantsev and Hay [7], we find zero-point and thermal corrections to attribute for less than 1 kcal/mol in the exchange reaction (2) which is smaller than our uncertainty in Gibbs energies and therefore, they are not included in the calculations. Although the experimental data on Cm/Gd separation is scarce, the calculated values are expected to be within 0.2 kcal/mol to Am/Eu or Cm/Eu separation (see [1] Fig. 6).
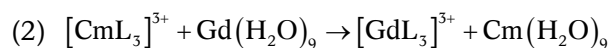
Results

In earlier studies we built force field models for the Th(IV) and Cm(III) aquo ions adjusted to binding energies at the MP2 or CCSD(T) level [22, 23].

With the same approach we have started to compute reference points for a Cm(III) and Gd(III) force field describing the interaction with N-donor and O-donor based ligands. Here we consider the following ligands:

- *N,N,N′,N′*-tetrakis[(6-carboxypyridin-2-yl)methyl]ethylenediamine (TPAEN) [24] Fig. 1(a)
- *N,N,N′,N′*-tetramethyldiglycolamide (TMDGA) Fig. 1(b);
- bis-2,6-(5,6,7,8-tetrahydro-5,9,9-trimethyl-5,8--methano-benzo-1,2,4-triazin-3-yl)pyridine (CA-BTP) [25] Fig. 1(c);
- 6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-1,2,4-triazin-3-yl)pyridine (CyMe$_4$-BTP) [26] Fig. 1(d);
- 2,6-bis(1,2-diazin-3-yl)pyridine (BDP) [2] Fig. 1(e);
- 2,6-bis(1,2,4-triazin-3-yl)pyridine (BTP) [27] Fig. 1(f); R=H;
- 2,6-bis(1,2,4,5-tetrazin-3-yl)pyridine (BQP) [2] Fig. 1(g);
- 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (*n*Pr-BTP) [28] Fig. 1(f); R = *n*-propyl;
- 2,6-bis(5,6-diisopropyl-1,2,4-triazin-3-yl)pyridine (*i*Pr-BTP) [28] Fig. 1(f); R = iso-propyl
- 2,2′:6′,2″-terpyridine (TERPY) [29] Fig. 1(h);
- 6,6′-bis(1,2,4-triazin-3-yl)-2,2′-bipyridine (BTBP) [30] Fig. 1(i); R=H;
- 2,6-bis(5-(2,2-dimethylpropyl)-1H-pyrazol-3-yl)pyridine (C5BPP) [31] Fig. 1(j);
- bis([2,2′-bipy]-5-methyl)(phenyl)phosphine-sulfide (BPS) Fig. 1(k).

Structures for all above ligands are depicted in Fig. 1. The TMDGA ligand was chosen as a representant for the TODGA [32] ligand.

Determined average bond-distances are listed in Table 1. Also, for the 3-dentate ligands, the difference in distances between the cap- and prism-positions Δr are listed. In all cases, the bond-lengths for the Gd complexes are shorter by 2–5 pm compared to the Cm counterparts. Differences $\Delta\Delta r$ are smaller, within 1–2 pm. Note, that the values for the corresponding aquo ions on the same level of theory are $\Delta r_{Cm} = 2$ pm and $\Delta r_{Gd} = 3$ pm. In accordance with shorter bond-lengths, the binding energies (BEs) listed in Table 2 are lower for all Gd-complexes compared to their Cm equivalents. Hence for the reaction (2), energy is consumed exchanging the lanthanide for the actinide ion in the ligand-complex.

$$(2) \quad [CmL_3]^{3+} + Gd(H_2O)_9 \rightarrow [GdL_3]^{3+} + Cm(H_2O)_9$$

However, in gas-phase, the nona-coordinated Gd aquo ion is more stable by 17.7 kcal/mol compared to Cm, resulting in a positive ΔE_g for all ligands at hand except TMDGA, which is in accordance with experimental findings. It should also be noted that despite the BDP ligand having a considerably lower BE than BTP and BQP, its 1:3 stability constant is lower and also highly pH-dependent [2].

Addition of the solvation energies G_{sol} shifts the equilibrium in favor of the actinide by 0.8–2.5 kcal/mol, induced by a higher dipole polarizability of the Cm(III) ion (1.165 Å^3 [23]) compared to Gd(III)
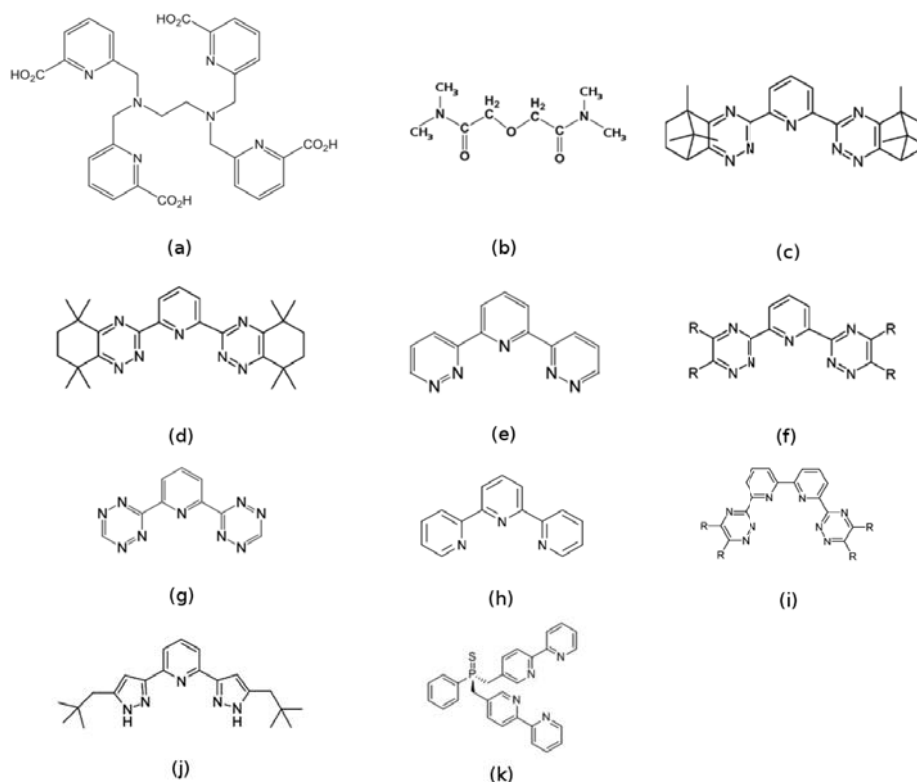
Fig. 1. Molecular structure of the investigated extracting ligands.

Table 1. Comparison of the obtained bond distances in Å for the Cm(III) to the Gd(III) complexes. Δr denotes the differences in cap- and prism-distances for the nona-coordinated complexes

	Cm-N	Cm-O	Δr	Gd-N	Gd-O	Δr
BDP	2.63	–	0.06	2.59	–	0.05
BTP	2.62	–	0.01	2.58	–	0.00
BQP	2.61	–	0.00	2.59	–	−0.01
iPr-BTP	2.63	–	0.00	2.59	–	−0.01
nPr-BTP	2.62	–	0.01	2.58	–	0.00
CyMe$_4$	2.63	–	0.00	2.59	–	−0.01
CA-BTP	2.62	–	0.01	2.58	–	−0.01
TMDGA	–	2.50	0.21	–	2.45	0.20
TERPY	2.65	–	0.01	2.62	–	−0.01
C5BPP	2.62	–	0.10	2.58	–	0.10
TPAEN	2.71	2.53	–	2.68	2.48	–
BTBP	2.57	–	–	2.52	–	–
BPS	2.64	–	–	2.60	–	–

Table 2. Comparison of binding energies in kcal/mol for the Cm(III) to the Gd(III) complexes in gas-phase and solution approximated using a continuum model to experimental data of the exchange reaction (2). Most experimental values correspond to the Am/Eu or Cm/Eu separation

	BE(Cm)	BE(Gd)	ΔE_g	ΔG_{aq}	Exp.
BDP	−734	−749	2.0	4.1	1.0 (Am/Eu) Et-BDP [2]
BTP	−686	−702	2.3	4.6	2.0 (Cm/Eu) nPr-BTP [33]
BQP	−605	−620	2.4	4.5	1.3 (Am/Eu) nPr-BQP [2]
iPr-BTP	−738	−753	2.3	5.0	2.0 (Cm/Eu) [33]
nPr-BTP	−741	−756	2.3	3.9	2.9–3.2 (Cm/Eu) [28, 30]
CyMe	−738	−753	2.5	5.5	4.1 (Am/Eu) [25]
CA-BTP	−756	−771	2.1	5.1	2.7 (Am/Eu) [25]
TMDGA	−734	−754	−2.7	−0.7	−0.9 (Am/Eu) TODGA [24]
TERPY	−702	−718	0.9	2.0	1.2–1.3 (Am/Eu) [34]
C5BPP	−725	−741	1.5	3.7	2.7 (Am/Eu) [31]
TPAEN	−665	−680	2.7	5.2	1.3 (Am/Eu) [24]
BTBP	−659	−676	1.2	2.0	2.4 (Cm/Eu) tBuC2-BTBP [1]
BPS	−674	−690	1.5	3.8	–

$(0.79 \text{ Å}^3$ [35]). In most cases the gas-phase ΔE_g are closer to the experimental values underlining the difficulties in the COSMO approach. It has to be highlighted however, that the order of separation factors BTP > BQP > BDP is only reproduced correctly after addition of the continuum model. When comparing to experimental results we select the values corresponding to the most acidic solutions. Hereby, an uncertainty is introduced as we did not consider any counterions like nitrate in our calculations.

For the 4-dentate ligands, we consider no solvent molecules in the first coordination sphere of the ion. Although gas-phase minima can be found on the potential surface including one water molecule in direct contact with the metal ion, it is unclear whether it is present in the solution. BEs for the different 4-dentate ligands considered here are very close. Their solvation energies G_{sol} differ significantly as their molecular structure offers different interactions with the solvent (Table 2).

Conclusions

In this study, we have investigated the gas-phase structure and energies of Cm(III) and Gd(III) complexes with various N- and O-donor ligands. Our main objective was to obtain reliable MP2 binding energies as reference points for future force-field adjustments since most studies rely on DFT data only. Especially for Gd(III) quantum chemical data is scarce. To estimate the influence of the solvent, solvation energies have been calculated using a polarizable continuum model approach. It was shown that the absolute gas-phase binding energy is no direct indicator for complex stability. All results showed fair agreement with experimental data, although uncertainties of the different methods do not allow definite assessment when comparing different ligands. Especially dynamic effects are not considered within the continuum approach which are assumed to play a major role. Also, nitrate co-extraction will have to be investigated theoretically, as the efficiency in the ligands separation properties strongly depends on it. The present study combined with the development of accurate force fields paves the way towards such investigations as their reliability and independence strongly depends on the accuracy of the reference data they are adjusted to. Molecular dynamics simulations based on force field approaches allow the study of thermodynamical effects of different systems and solvents.

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