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Toward a Clear-Cut Vision on the Origin of 2,6-Di(1,2,4-triazin-3-yl)pyridine Selectivity for Trivalent Actinides: Insights from Theory

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Although BTP (2,6-di(1,2,4-triazin-3-yl)pyridine) has been widely evidenced as the most effective nitrogen ligand for the selective complexation of trivalent actinides from lanthanide counterparts, the origin of its selectivity is still an open question. Neither experimental data nor theoretical calculations have been able to rationalize the role of covalency in real experimental BTP complexes. We show herein with DFT calculations on $[M(BTP)_3]^{3+}$ (M = La, U, Cm, Gd) that, even if back-bonding effects are significant in the U–BTP bond, it is the contrast of donation on 6d and 5f Cm^{III} orbitals that explains, at least in part, its selective complexation to BTP.

Introduction

Current environmental and energetic concerns have led the partitioning of minor actinides An^{III} (americium and curium) from lanthanides Ln^{III} (europium) to be at the forefront of nuclear waste disposal research. Much interest has thus been devoted to design discriminating ligands able to coordinate actinides selectively. However, close similarities between actinide and lanthanide chemical properties, e.g., similar ionic radii and coordination numbers, make their separation a difficult problem. The higher spatial expansion of 5f actinide orbitals with respect to the 4f lanthanide orbitals nevertheless opens possibilities to discriminate them through their relative hardness. Numerous soft donor ligands bearing S, O, P, or N atoms have thus been tested and proved to favor binding An^{3+} over Ln^{3+} (see, for instance, refs 1−5). To minimize secondary solid waste, recent research has been focused on ligands respecting the 'CHON principle', that is molecules containing only C, H, O, and N atoms. The first significant step forward this goal was performed in 1999 by Kolarik et al.[6] who synthesized the most selective nitrogen extractant to date, the so-called BTP (alkylated 2,6-di(1,2,4-triazin-3-yl)pyridine) sketched in Figure 1. Why BTP is so effective is nevertheless still unclear, especially as experimental data are rather scarce. Its remarkable coordination mode, that is, 1:3 metal-to-ligand ratio with no inner solvent molecules, has been identified in several papers,[7−9] stressing the role of entropy effects. The latter are, however, not sufficient to explain BTP selectivity since terpyridine can feature a similar coordination mode with a much lower selectivity.[7] An appreciable decrease of the $U-N_{BTP}$ distance with respect to $Ce-N_{BTP}$ counterpart was notably recorded and assigned to a stronger covalency with U^{III}. Indeed, whereas Ln^{III} systems are purely ionic, significant electron back-donation can occur from U^{III} 5f orbitals to π^* levels of π-acceptor ligands.[7] However, when considering radionuclides really involved in the spent fuel as Cm^{III} and Am^{III},

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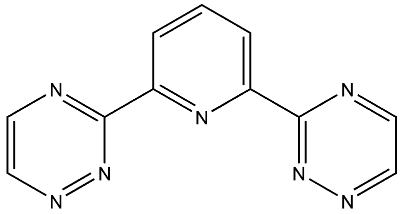

Figure 1. Structure of BTP (2,6-di(1,2,4-triazin-3-yl)pyridine).

the origin of An/Ln discrimination, and thereby the nature of the metal−ligand bonding, seems far more obscure. In recent EXAFS studies, Denecke et al.[8] did not find any structural differences between $[\mathrm{Cm(BTP)_3}]^{3+}$ and its $\mathrm{Eu^{III}}$ analogue but observed the direct formation of the 1:3 Cm system whereas europium forms several intermediate species. Therefore, even though enthalpy factors are of importance in actinide-selective extraction,[10] their very nature is not straightforward to experimentalists.

There is thus a strong need, due to the major interest of both fundamental aspects of the rare earth coordination chemistry and of potential applications of BTP, to carry out more advanced studies. The theoretical approach naturally lies within this perspective since it has already enabled the shedding of light on f-element molecular system properties[10−15] and can moreover provide a very fine description of the metal−ligand bond.[12] However, reproducing large heavy metal complexes theoretically remains challenging since they combine several drawbacks: open shells, strong electron correlation, and relativistic effects. Special care must thus be taken concerning orbitals occupancy, an often fuzzy aspect in quantum chemical studies on these compounds.

We thus present herein a comprehensive study of $\mathrm{La^{III}}$, $\mathrm{U^{III}}$, $\mathrm{Cm^{III}}$, and $\mathrm{Gd^{III}}$ BTP complexes, successively focusing on structural, energetic, charge, and orbital aspects. Such systems were chosen in agreement with available experimental data, as well as for their chemical interest: La and U have similar ionic radii but feature quite different covalency effects. As they are already well characterized at the experimental level, they can be viewed as a benchmark for the computational aspect of this work. Curium is involved in the nuclear spent fuel but, to our knowledge, very few structural data exist on $[\mathrm{Cm(BTP)_3}]^{3+}$.[8] The best approach would have been to make the comparison with the $\mathrm{Eu^{III}}$ BTP, as it is used for separation factor tests and as EXAFS data are available,[8] but we were not able to reach convergence. Its neighbor $\mathrm{Gd^{III}}$, which has the same f^7 occupancy as $\mathrm{Cm^{III}}$, was considered instead. Actually, covalency effects have already been suggested for related compounds[10,14,15] but they were then extremely low, almost within the computational uncertainties. Recently, Miguirdichian et al.[10] performed a thermodynamic study on $\mathrm{Ln^{III}}$ and $\mathrm{An^{III}}$ complexes of ADTPZ, a tripodal nitrogen ligand with one central 1,3,5-triazine and two lateral pyridines. Their DFT calculations pointed out some donation on d and f metal orbitals, but they were not able to make a clear distinction between lanthanides (La, Nd, Gd) and actinides (Pu, Am, Cm) complexes. Similar trends were found by Guillaumont[15] when considering $[\mathrm{M(MeBTP)(H_2O)_6}]^{3+}$ (M = La, Ce, Nd, U, Pu, Am, Cm) complexes at the DFT level. In Denecke and coworkers EXAFS studies,[8] $\mathrm{Cm^{III}}$ and $\mathrm{Eu^{III}}$ BTP complexes were investigated theoretically, but only structural aspects were then examined. Therefore, besides providing the first analysis of the bonding in $[\mathrm{M(BTP)_3}]^{3+}$ systems, our study is also the first theoretical proof of the role of covalency for heavy $\mathrm{An^{III}/Ln^{III}}$ discrimination.

Theoretical Basis

The ADF package (release 2004.01)[16−18] was used to perform all calculations except the natural bond orbital (NBO) and natural population (NPA) analyses.[19] The NBO approach is indeed not implemented yet in the ADF code for open-shell systems and was thus carried out with the Gaussian 03 suite of programs.[20]

Trivalent rare earths generally experience a weak ligand field, so the highest spin multiplicity was applied each time, namely quartet for $\mathrm{U^{III}}$ and octuplet for $\mathrm{Cm^{III}}$ and $\mathrm{Gd^{III}}$. All calculations were performed in vacuum since there is no solvent molecule in the first coordination sphere. Moreover, the complex being relatively hydrophobic, we may also assume that solvent molecules have little influence on the complex structure. This aspect was nevertheless tested with a continuum dielectric water model, as it should be adapted to take into account electrostatic effects due to the high cationic charge and we thus used the Conductor-like Screening Model of solvation (COSMO).[21−23] Radii were taken from Allinger et al. MM3 calculations[24] with a scaling factor of 0.833, as commonly suggested.[25] Chosen radii and results for $[\mathrm{La(BTP)_3}]^{3+}$

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Table 1. Calculated Metal−Ligand Distances for $[M(BTP)_3]^{3+}$ Systems[a]

	constrained geometries		fully relaxed geometries		ionic radius for the M^{3+} cation,[b] Å
	$d(M-N_{py})$, Å	$d(M-N_{tz})$, Å	$d(M-N_{py})$, Å	$d(M-N_{tz})$, Å	
$[La(BTP)_3]^{3+}$,	2.70 (2.67)[c]	2.67 (2.63)[c]	2.74 (2.67)[c]	2.69 (2.63)[c]	1.06
$[U(BTP)_3]^{3+}$,	2.58 (2.54)[c]	2.56 (2.54)[c]	2.54 (2.54)[c]	2.56 (2.54)[c]	1.06
$[Cm(BTP)_3]^{3+}$,	2.59 (2.57)[d]	2.57 (2.57)[d]	2.61 (2.57)[d]	2.61 (2.57)[d]	0.98
$[Gd(BTP)_3]^{3+}$,	2.58 (2.56)[e]	2.57 (2.56)[e]	2.58(2.56)[e]	2.59(2.56)[e]	0.94
$[La(BTP)_3]^{3+}$, Cosmo H_2O	2.69	2.67			1.06
$[U(BTP)_3]^{3+}$, Cosmo H_2O	2.57	2.56			1.06

[a] Experimental values are mentioned in parentheses. Ionic radii for a coordination number of 6 are also indicated. N_{py}: pyridine nitrogen; N_{tz}: triazine nitrogen. [b] From ref 35. [c] Crystal structures of $[La(Me\text{-}BTP)_3]^{3+}$ and$[U(Pr-BTP)_3]^{3+}$, ref 7. [d] EXAFS values for $[Cm(Pr\text{-}BTP)_3]^{3+}$, ref 8. [e] EXAFS values for $[Eu(Pr-BTP)_3]^{3+}$, ref 8.

and $[U(BTP)_3]^{3+}$ using the COSMO model are fully detailed in Supporting Information.

Concerning ADF calculations, the scalar relativistic ZORA approach associated with the Becke Perdew GGA functional[26] was applied since several papers have already validated this method as a proper way to describe the f-element complex ground states.[11,27] Adapted triple-ζ plus two polarization functions STO basis sets (only one polarization function for f elements) were used for the description of the valence part of all atoms and we kept their core frozen up to 4d/5d for lanthanides/actinides and up to 2p for chlorines and 1s for remaining carbon and nitrogen atoms. The ADF package also supplies an energetic decomposition of the metal−BTP bonding into chemically useful terms. Such an analysis is based on the transition-state method developped by Ziegler and coworkers.[28] To sum up, we have introduced the ligand as a fragment (3 BTP) and studied its interaction with the metal center. Note in particular that the ligand being described by only one fragment, we get rid of the interaction between the three BTPs and only the metal−3BTP interaction is considered. This energy is then decomposed into

$$\Delta E_{\text{bonding}} = \Delta E_{\text{steric}} + \Delta E_{\text{orb}}$$

where ΔE_{steric} is the steric interaction energy between the metal and the three BTPs and ΔE_{orb} is the orbital contribution to the metal−3BTP bond. Actually, the steric energy can be further decomposed into a destabilizing term ΔE_{Pauli}, the electronic repulsion due to the Pauli principle, and ΔE_{elec}, the stabilizing electrostatic energy between the metal and the three BTPs. Similarly, the orbital part includes both a polarization term due to the reorganization of the metal and ligand electronic densities when complexing and some possible covalency if their orbitals overlap. Unfortunately, these two terms cannot be quantified separately. When dealing with high-symmetry systems, donation and back-donation can in principle be separated through a partitioning of the orbital energy into the contributions from distinct irreducible representations. This analysis cannot be performed for our complexes since, as we respect the experimental structure, there is no symmetry at all. Finally, BSSE corrections were found to be low enough in comparison to the computed ΔE values, on the order of 0.3 eV.

The Mulliken[29] charges and populations are generally too low, thus suggesting too-covalent interactions, although global trends are, in contrast, often well reproduced. The NPA technique has several times proved to be reliable,[12,30] notably for f-element complexes, and was thus applied with the Gaussian03 package. Note that charge differences from one BTP to another are very low, so mean values are reported. Careful consideration was dedicated to check orbital filling since the Gaussian code can sometimes give wrong occupancies for heavy open-shell metals. As far as possible, we used similar parameters to ADF calculations, that is, the BP86 functional with the 6-31G* basis set for nitrogen, carbon, and hydrogen atoms. The metal cation was described with small core quasirelativistic Stuttgart pseudopotentials.[31]

Results and Discussion

$[La(Pr-BTP)_3]^{3+}$ and $[U(Pr-BTP)_3]^{3+}$ crystallographic structures[7] were used as starting points for our optimizations, while the ligand geometry in $[U(Pr-BTP)_3]^{3+}$ was taken for $[Cm(BTP)_3]^{3+}$ and $[Gd(BTP)_3]^{3+}$. Each time, only metal−nitrogen distances were relaxed to avoid cumbersome calculations. For similar reasons, we removed propyl susbstituants from triazine rings. Actually, their external position has been proved to hardly affect the complex structure.[7,8] To ensure that our geometries were not fortuitous, they were fully relaxed with the same starting points as for constrained optimizations (XR structure of $[U(BTP)_3]^{3+}$ for U, Cm, and Gd complexes and XR structure of $[La(BTP)_3]^{3+}$ for the La system). Results, listed in Table 1, sometimes show a little increase in M−N distances, from 0.02 to 0.04 Å, but negligible angular variations. Corresponding Cartesian coordinates are given in the Supporting Information. In particular, for Cm and Gd complexes, starting full optimizations from the La−BTP_3 X-ray structure provide similar geometries as that obtained from U−BTP_3. Very low changes, within the computational range of error (∼0.02 Å), were also found when adding continuum water solvent on La and U−BTP complexes (Table 1). Therefore, to be as close as possible to experimental data, following geometrical, energetic, charges, and orbital analyses are based on constrained optimized structures.

Corresponding M−N distances are in good agreement with experimental findings (Table 1) since the mean error does not exceed 0.04 Å. As observed in crystal structures,[7] strong back-bonding effects in the U complex result in a shortening of 0.11 Å of the U−N distance with respect to the La−N

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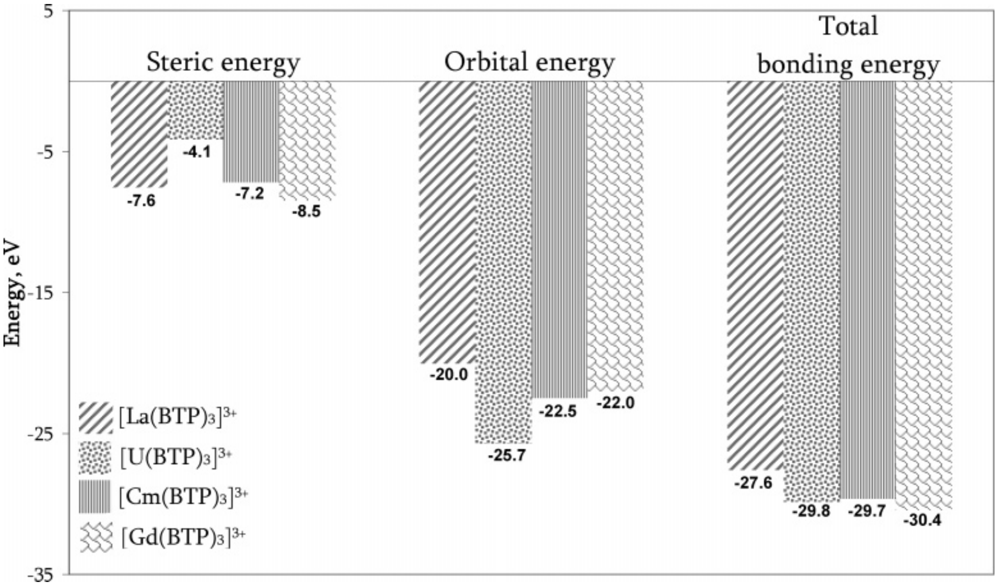

Figure 2. Energetic decomposition of the different contributions involved in the complexation process of M^{3+} by three BTP.

bond. Of special interest is that a very good accord is obtained with EXAFS values[8] for $[Cm(BTP)_3]^{3+}$ but a comparison with other metals looks more ambiguous: although having a smaller ionic radius than U^{III} (see Table 1), the Cm complex features similar M$-$N distances, thus indicating that covalency may be lower therein. Comparable arguments could be given for $[Gd(BTP)_3]^{3+}$, noting that the ionic radius of Gd^{3+} is lower than that of Cm^{3+}. Unfortunately, no experimental geometry is available for the Gd complex to validate computed Gd$-$N values. We can nevertheless point out that no structural difference was observed between Eu and Cm BTP systems using EXAFS measurements and thus that our computed distances seem reasonable. Experimental distances obtained for nearby elements (d_{M-N} $[Sm(BTP)_3{}^{3+}] = 2.57$ Å; d_{M-N} $[Eu(BTP)_3{}^{3+}] = 2.56$ Å)[8,9] support this conclusion.

In this regard, the metal$-$BTP bonding energy can be divided into chemically meaningful terms as discussed in the Theoretical Basis section. This energetic decomposition provides insights into the balance of the different phenomena at stake when complexing the isolated cation to three BTPs. We remind the reader that, within this scheme, the resulting total bonding energy is divided into two terms, the steric energy and the orbital energy, as displayed in Figure 2. It is first useful to note that in the absence of counterions the high metallic charge induces a significant polarization of the ligands that strongly contributes to the computed orbital energies. However, it seems reasonable to assume that polarization is roughly the same for the U, Cm, and Gd complexes, as their M$-$N distances are similar, and that the evolution of their orbital energies consequently follows that of covalency. In contrast, La$-$BTP distances are longer and polarization must then be lower. In this manner, $[U(BTP)_3]^{3+}$ is found to be particularly stable (-29.8 eV) due to an appreciable covalency and, in particular, strong back-bonding effects.[7] U$-$N distances being short relative to U^{3+} radius, the Pauli repulsion becomes highly destabilizing and explains the low steric term (-4.1 eV). In contrast, despite a strong steric energy of -7.6 eV, the La compound features the lowest bonding energy (in absolute values) because of a weak orbital part (-20.0 eV). More interesting are the differences computed for Cm and Gd compounds. The gadolinium cation appears to be far enough from the ligand to minimize its Pauli repulsion while maintaining an orbital part significantly higher than for lanthanum (-22.0 eV), and $[Gd(BTP)_3]^{3+}$ is thus found to be the most stable (-30.4 eV). In agreement with the relative ion size, the curium complex logically presents an enhanced Pauli repulsion, and thus, a lower steric term (-7.6 eV). The orbital energy in contrast strengthens with respect to the Gd analogue (-22.5 eV), which confirms the previous assumption of stronger covalent effects in the Cm system. We would like here to focus the reader's attention on the fact that computed total bonding energy values are not meaningful insofar as a complete thermodynamic scheme should be applied to compare the relative stability of the complexes studied. In particular, the dehydration process should be taken into account to consider rigorously this aspect but this is out of the scope of our study.

The charge analysis substantiates these energetic data. Although the Mulliken approach[29] can provide correct global trends, the NPA technique is much more reliable[12,30] and often gives more meaningful results. Mulliken charges are thus given in the Supporting Information (Table SI4) for comparison only while our discussion is based on NPA results listed in Table 2 ('NPA charge' section). On the whole, electrons are withdrawn from the BTP ligand whose charge is always found to be positive while the metal charge decreases ($q_M < 3$) as the cation retrieves electrons. This trend is particularly pronounced for $[Cm(BTP)_3]^{3+}$ whose metallic charge is appreciably smaller (2.10 $|e^-|$, NPA) than for the La and Gd counterparts (2.44 $|e^-|$ and 2.52 $|e^-|$, NPA), suggesting a strong donation from BTP to the Cm cation. A similar reasoning for the uranium system is in contrast a bit more complex. Donation and back-donation are superimposed and affect charges in opposite ways. The resulting U^{III} charge of 2.56 $|e^-|$, that is 0.12 $|e^-|$ higher

Table 2. NPA Charges and NBO Orbital Populations (Performed with Gaussian03) for $[M(BTP)_3]^{3+}$ Systems[a]

	$[La(BTP)_3]^{3+}$	$[U(BTP)_3]^{3+}$	$[Cm(BTP)_3]^{3+}$	$[Gd(BTP)_3]^{3+}$
	NPA Charges			
q_M, $\lvert e^- \rvert$	2.44	2.56	2.10	2.52
q_{BTP}, $\lvert e^- \rvert$	0.19	0.15	0.30	0.16
Δq_{Npy}, $\lvert e^- \rvert$	−0.23	−0.28	−0.30	−0.25
Δq_{Ntz}, $\lvert e^- \rvert$	−0.29	−0.27	−0.25	−0.24
	NBO Orbital Populations			
Δn(s)	0.21	0.27	0.28	0.25
Δn(p)	0.02	0.01	0.01	0.02
Δn(d)	0.19	0.26	0.22	0.20
Δn(f)	0.16	−0.37/0.29	0.35	0.02

[a] Npy and Ntz refer to bonding pyridine and triazine nitrogen atoms, respectively. Δq represents charges differences between the complexed and the isolated BTP. Δn is the population difference for the s, p, d, and f levels of the metal center between the complex and free cation.

than for La^{III}, shows that back-donation is predominant, a pattern that will be confirm below in the orbital analysis.

A detailed study of the charge distribution within pyridine and triazine BTP rings seem to us inappropriate given that BTP being conjugated, corresponding populations are distributed all over the ligand. BTP conjugation indeed results in large density fluctuations, fairly similar whatever the metal is—bonding nitrogen atoms withdraw electrons from the less electronegative carbon and hydrogen atoms and transfer them partially to the metal. As attested by Δq_{Npy} and Δq_{Ntz} values in Table 2, they however manage to keep an appreciable amount of density. The interaction with the positive metal center is considerably strengthened and explains the great stabilizing role of the polarization term in the previous energetic analysis. In particular, this could account for the surprising high charge found on gadolinium (2.52 $\lvert e^- \rvert$). As suggested in the energetic analysis, Gd being closer to the ligand than La, the polarization is stronger. The lower charge on La (2.44 $\lvert e^- \rvert$) thus proves that the difference in the orbital term between Gd and La complexes is due to polarization and even that covalency may be higher in $[La(BTP)_3]^{3+}$.

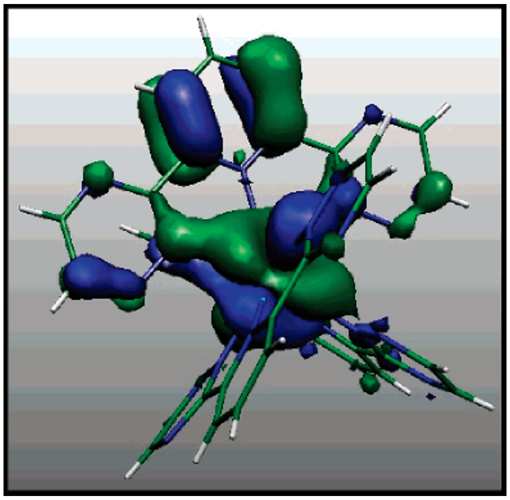

Figure 3. Visualization of donation effects for the $[Cm(BTP)_3]^{3+}$ complex.

Table 3. Total Contribution of Metal d and f Orbitals to BTP Levels Based on Boys−Foster Analysis

donation	$[La(BTP)_3]^{3+}$	$[U(BTP)_3]^{3+}$	$[Cm(BTP)_3]^{3+}$	$[Gd(BTP)_3]^{3+}$
d, α orbitals	0.36	0.60	0.48	0.45
d, β orbitals		0.46	0.31	0.39
f, α orbitals	−	0.27	−	−
f, β orbitals	−	0.10	−	−

Whereas early actinide 5f orbitals are fairly diffuse and close in energy to the 6d levels, the shell contraction with the atomic number makes the f levels of the second half of the actinide series deeper in energy, thus decreasing their interaction with the ligand. Therefore, although differences between La^{III} and U^{III} are quite evident experimentally, they become almost imperceptible when comparing Cm^{III} to Eu^{III} or Gd^{III} for instance. The advantage of performing a theoretical analysis notably lies in the possibility to have access to the orbital occupancy. Generally, levels with predominant f character in Ln and An complexes are located in the frontier orbitals. As far as they are partially filled, donation and/or back-donation can occur through a mixing between the metal and the ligand levels, and indeed, major back-bonding effects from singly occupied α 5f(U) (the three highest occupied α levels) to BTP π^* orbitals are observed in $[U(BTP)_3]^{3+}$, with an average of 18.6%. Actually, they superimpose to donation on d and f uranium levels: both α and β levels show around 2.5% of d(U) on 6 BTP orbitals as well as a low mixing of f(U) (1.5% in average on 4 α BTP levels). For the closed-shell $[La(BTP)_3]^{3+}$, back-donation is obviously excluded but there is nevertheless some donation on lanthanum d orbitals: 8 BTP-based levels indeed present a slight percentage of d(La), on the order of 1.5%. Similar behavior is found for Gd and Cm complexes (Figure 3), but due to the strong mixing between metal and BTP orbitals, it is actually easier to quantify donation through more advanced analyses. To this end, the Boys−Foster method,[32−34] implemented in the ADF package, provides a set of orbitals that are more localized in space than the canonic Kohn−Sham orbitals. As shown in Table 3, results globally support the previous orbital analysis with donation on metal d orbitals for the four systems. However, they do not account for the low curium charge revealed by both Mulliken and NPA analyses with respect to gadolinium as the amount of electronic transfer on metal d levels is similar for both complexes. Mulliken and, above all, NPA approaches have nevertheless proved many times to provide a reliable view on the evolution of charges within rare earths complexes. Therefore, to obtain a clearer picture of such donation effects, the NBO analysis was applied, and results are displayed in Table 2 ('NBO populations' section). We must first notice that, although this analysis has been performed with different calculation parameters (G03, BP86 with Gaussian basis sets), the consistency with the previous ADF orbital scheme is very good. In particular, we remind the reader that careful consideration was dedicated to obtain an orbital occupancy as close as possible between ADF and Gaussian03 calculations, and indeed, in agreement with ADF results, similar donation effects are found on La, Cm, and Gd d levels (around +0.2 $\lvert e^- \rvert$), while being slightly increased for uranium (0.26 $\lvert e^- \rvert$). The real differentiation between the

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four complexes actually relies on the metal f levels. Logically, as 4f (Gd) orbitals are very contracted, they hardly interact with the ligand, whereas such a mixing occurs for the softer lanthanum (+0.16 $|e^-|$). The balance between α and β levels is detailed for $[U(BTP)_3]^{3+}$ and confirms that back-donation (−0.37 $|e^-|$ on α spin−orbitals) is predominant over donation. Donation becomes really significant for the Cm complex for which up to 0.35 $|e^-|$ are transferred from BTP to curium f β spin−orbitals, thus explaining the exceptionally low metallic charge found with both Mulliken and NPA analyses. It is nevertheless advisable to consider such results with care as, with both ADF and Gaussian orbital analyses, no major donation on curium f β spin−orbitals is observed. We assume that the mixing between Cm vacant f orbitals and BTP is low enough to be negligible for an orbital analysis but, as it occurs on a large number of molecular orbitals, it finally results in a quite appreciable electronic transfer. Hence, even though it is quite hard to localize donation accurately, the fact still remains that covalency is clearly higher within the Cm−BTP bond.

Conclusion

The high selectivity of BTP toward trivalent actinides is a complex process that may be ruled by both entropy and enthalpy effects. Among the latter, our calculations indicate the major role of covalency through f and d metal levels. Experimental trends for La^{III} and U^{III} complexes are confirmed, i.e., a slight donation for both systems adding further to a strong back-donation for uranium. More interesting is that donation on f(Cm) orbitals seems to act as a determining factor in Cm^{III} selective complexation to BTP. The comparison with the Gd analogue supports experimental conclusions (EXAFS, ref 8) as both complexes feature the same geometry, but quantum chemistry calculations enable us to go further, showing that covalency is nevertheless higher within the Cm−BTP bond. Thus, our study once again shows how theoretical methods supply a powerful and fine means to interpret experimental findings.

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Supporting Information Available: Table SI1 (radii values for Cosmo calculations), Table SI2 (fully relaxed complexes coordinates), Table SI3 (complete results for Cosmo calculations), and Table SI4 (Mulliken charges). This material is available free of charge via the Internet at http://pubs.acs.org.

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