Enhancement in selectivity of trivalent Am over Cm by modulating donor centres of aza- macrocyclic ligands: An implication of their differences in bonding

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Research Article

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Enhancement in selectivity of trivalent Am over Cm by modulating donor centres of aza-macrocyclic ligands: An implication of their differences in bonding

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Keywords: minor actinide separation, soft donor, bonding, f-orbital, relativistic DFT
Abstract:

Efficient management of the high-level liquid waste (HLW) generated during the reprocessing of nuclear fuel involves mutual separation and transmutation of the minor actinides like Am and Cm, which are chemically very similar. In the present work, an in-silico analysis of the bonding of Am(III) and Cm(III) ions with donor center modulated azacrown based ligand, i.e., a ligand formed by replacing the four ‘O’s of the azacrown macrocycle in \( \text{N,N'}-\text{bis}[6\text{-carboxy-2-pyridyl}]-\text{methyl}]1,10\text{-diaza-18-crown-6} \) (L1) with four ‘S’s (L2) is carried out using relativistic density functional theory to develop a deeper understanding of the impact of both, soft donors as well as the cavity effects on the separation of these metal ions. The subtle differences in the bonding is brought about by the covalent interaction of the metal and the aza-macroyclic O and S donors. The electron donation from the ligand is mostly accepted in the metal 6d orbitals and minimally to the 5f orbitals. But the f-orbital participation plays the crucial role in bringing about the subtle difference in the bonding between Am(III) and Cm(III) ions with the ligands. The trivalent Cm ion with half-filled initial f\(^7\) configuration shows resistance in participating in bonding as was observed from NPA, QTAIM, NBO and DOS analyses. Whereas, the Am(III) ions having f\(^6\) configuration are eager to accept f-electrons to achieve the stable half-filled configuration. The energetics elucidated that both L1 and L2 ligands are Am selective. But the extraction capacity and selectivity is higher for the L2 ligand. The Am selectivity can be attributed to the significant covalent interaction of S donors which have better electron donating capacity (than O) to the electron deficient Am(III) ion. This study is anticipated to throw some light on the implication of the bonding features on their separation.
Introduction:

Nuclear energy is a green source of energy making it one of the most environment friendly options. However, to reduce the burden on future generations and to pave a path towards sustainable development via this energy route, efficient management of the high-level liquid waste (HLW) generated during the reprocessing of the nuclear fuel, needs to be addressed[1]. The HLW mainly consists of the unreacted Uranium and Plutonium. Along with the fission products, activation products are also encountered in the HLW. In the nuclear reactor with Pu and U fuels, subsequent neutron capture reactions lead to the formation of the minor actinides like Americium, Curium, Berkelium, Californium and so on. The concentrations of the minor actinides placed later in the period, tend to fall exponentially due to successive decrease in the concentration of the parent, rendering Am and Cm the prominent ones[2]. The reprocessing flowsheet includes, (i) recovery of the unreacted fissile U and Pu, (ii) separation of the remaining actinides from the lanthanide fission products, (iii) mutual separation between the minor actinides mentioned above[3–5]. Presently, the widely used module for management of HLW is its immobilisation into inert glass matrix units and their long term storage. However, the maintenance of such units during the long term storage is a herculean task because of its radioactive content. Removal of the long lived α-emitting radionuclides, mainly the minor actinides, through partitioning and transmutation, can help in reducing the storage duration. The second and third steps of reprocessing, aim towards preparation of targets for efficient transmutation of these long lived minor actinides, especially the Am isotopes[2, 6]. But the aforementioned steps, particularly the third one, are extremely difficult to carry out because these metals possess nearly identical chemical properties[7]. Trans-plutonium actinides have lanthanide-like chemistry, as the 5f orbital tends to become increasingly localized upon moving across the period[8]. The predominant trivalent oxidation state of these heavy actinides, coupled with the nearness in their ionic radii with the adjacent actinide ions and the lanthanides, calls for higher demands on ligand specificity for their separation. The higher relative diffusivity of the 5f orbitals compared to 4f enables more covalent interactions of actinides with soft donor ligands compared to those seen in the equivalent lanthanide complexes[9]. But for the adjacent actinide ions, the differences in the diffusivities of the corresponding 5f orbitals is negligible and hence, their separation becomes further challenging as compared to the intergroup separation of trivalent actinides and lanthanides. Several mixed donor ligands with N, P and S donor sites have been explored both experimentally and theoretically for this purpose including bis(2-ethylhexyl)phosphoric acid, 2,9-bis(1,2,4-triazin-3-yl)-1,10-phenanthroline, bis-(chlorophenyl)dithiophosphinic acid, etc[5, 10–15]. In addition to the above mentioned ligands, macrocyclic ligands such as crown ethers with hydrophilic groups are also used for the separation of transplutonium actinides[16, 17]. Presence of electron-
donating atoms like O, N, P, S in crown ether derivatives helps them to form stable complexes with these metal ions and their different cavity sizes provide different coordination environment, thereby invoking selectivity. N,N’-bis[(6-carboxy-2-pyridyl)-methyl]-1,10-diaza-18-crown-6 and N,N’-bis[(6-methylphosphinic-2-pyridyl)methyl]-1,10-diaza-18-crown-6 were found to have higher preference for Am$^{3+}$ over Cm$^{3+}$ in aqueous solution. It was also theoretically established that the bonding of the Am or Cm ions to the ligands is predominantly via the carboxylate and phosphinate units respectively and the selectivity is more for the latter ligand, but the extraction capacity is higher for the former[17]. In the present work, an in-silico analysis of the bonding of trivalent Am and Cm ions with donor center modulated azacrown based ligand, i.e., a ligand formed by replacing the four ‘O’s of the azacrown macrocycle in N,N’-bis[(6-carboxy-2-pyridyl)-methyl]-1,10-diaza-18-crown-6 (L1) with four ‘S’s (L2) is carried out using relativistic density functional theory. Attributing the preference of marginally softer trivalent Am over Cm for soft donor ligands only to the favourable soft-soft interaction is debatable, unlike in the case of lanthanide-actinide separation. Hence, a deeper understanding of the fundamental differences in bonding of the Am and Cm ions with these ligands, which have the impact of both, soft donors as well as the cavity effects, is expected to throw some light on the implication of the bonding features on their separation.

**Computational Details:**

In this study we have tried to understand the bonding interactions of the chemically similar Am$^{3+}$ and Cm$^{3+}$ ions with the two ligands in their deprotonated forms, (i) N,N’-bis[(6-carboxy-2-pyridyl)methyl]-1,10-diaza-18-crown-6 (L1) and (ii) computationally synthesised ligand where the four ‘O’ atoms of the crown ring of L1 are replaced by ‘S’ atoms, named L2 [Fig.1].

![Fig.1 Structures of ligands L1 and L2](image)

The initial geometry of the L1 was obtained from the study by Liu et al[17]. They have established it to be the minimum energy conformer amongst the other possible structures. In the same structure, the crown ether O’s were replaced by S to obtain the initial structure for L2. It was observed in the previous studies that the (δλδ)(δλδ) conformers of the Am and Cm complexes of L1 is most stable amongst the other possible ones[16, 17]. The initial structures of these complexes were obtained from the literature by Jensen et al[16]. Similar initial geometries of
the Am/Cm complexes with L2 were prepared by replacing the crown ether O’s by S. Throughout the study, a septet high spin ground state ($I^\pi$) for Am based systems and octet high spin ground state ($I^\pi$) for Cm based systems were considered.

Geometry optimizations of all the structures were carried out in gas phase with tight energy convergence criteria (10$^{-8}$E$_h$) using the pure-GGA BP86 functional[18, 19]. def2-TZVP[20] basis set and def-TZVPP[21] basis set, were used for describing the valence electrons of the light elements and Am and Cm respectively. Core electrons of the heavy atoms were modelled by a relativistic small-core effective core potential (SC-ECP)[22, 23]. Absence of imaginary frequencies confirmed that the optimized structures had reached the minimum energy. These analytical frequency calculations were carried out with the AOFORCE module of TURBOMOLE v7.2[24]. Single point energy calculations were performed at a higher level of theory [B3LYP[25, 26]/def2-TZVP[20]/(def-TZVPP)/scalar ZORA[27, 28]] with the optimized molecular geometries using ORCA 3.0.3[29] for achieving better accuracy. Zero-point energy correction was considered for obtaining the Gibbs free energies of each component of the complexation reactions. For both geometry optimisation and single point energy calculations the resolution of identity (RI) (for optimization) and RIJCOSX[30] (for single point) approximations were employed along with the corresponding auxiliary basis sets to achieve optimum computational efficiency. Spin-orbit coupling effects were not considered in this study.

Implicit solvation effect was addressed by using the conductor-like polarisable continuum model (CPCMC)[31, 32] as implemented in ORCA 3.0.3[29]. Density functionals for geometry optimization (BP86) and single points (B3LYP) were chosen based on previous research, which suggested that BP86 provides more accurate structural parameters, while B3LYP is more suitable for calculating the energies[33].

Frontier Molecular orbital (FMO) analysis was carried out to recognize the stabilities and extents of metal orbital participation in the complexes. For partial charge analysis, Natural population analysis (NPA)[34, 35], which is reported to work better in describing the bonds with minimal basis-set dependence, was carried out, along with computation of atoms-in-molecule charges. QTAIM descriptors like electron density ($\rho$), laplacian of the electron density ($\nabla^2 \rho$) and total energy density (H(r)) were analysed to get an insight into the ionic or covalent nature of the metal-donor bonds. The natures of the bonds were analysed by partitioning the molecular electron density ($\rho(r)$) region at the zero flux surface, thereby describing the bond formation by a (3, − 1) bond critical point (BCP)[36, 37]. The properties at the BCP provide a quantitative understanding on the extent of covalency in the metal donor bonds. Furthermore, Wiberg bond indices (WBIIs) and the delocalization indices (DI) were computed as a measure of the shared electron density between the bonded atoms. Natural bond orbitals (NBO)[35] were
analysed to understand the extent of participation of metal and ligand orbitals during bonding. NBO analysis was carried out using the GENNBO module of the ADF software, which links the same to NBO 6.0 program[38]. Negligible spin contamination was noted for all the systems [Table-S1]. Further, to analyse the energetic contributions associated with the bonding of the metal ion and ligand fragments, energy decomposition analysis (EDA)[39] was performed with the optimized structures at the B3LYP[25, 26]/TZ2P[40]/scalar-ZORA[27] level. In EDA, the bonding energy (ΔE_{bond}) of a complex is decomposed into electrostatic (ΔE_{elec}) and orbital (ΔE_{orb}) interactions, which are stabilizing in nature; and Pauli exchange interaction (ΔE_{Pauli}), which is repulsive. Further, the orbital interaction term ΔE_{orb}, was decomposed by applying the extended transition-state (ETS) theory in combination with the natural orbitals for chemical valence (NOCV) method[41] to obtain the deformation channels of the electron densities. All these calculations, unless stated otherwise, were carried out using ADF 2017 software[42].

Results and Discussions:

(i) Geometry and Frontier Molecular Orbital (FMO) analysis of the ligands L1 and L2

Both the ligands, L1 and L2 have aza-crown (like) macrocyclic units with two dipicolinate arms as is seen in their optimised structures in Fig 2. In case of L2, the O atoms of the aza-crown unit are replaced by sulphur atoms. All the heteroatoms in the aza-crown ring in L1 are positioned at about 112° above or below the planes of the adjacent C atoms. Whereas, in case of L2, although the ring Ns maintain their position with respect to the adjacent Cs, but, the S atoms have shifted up or down by 10°-30° in comparison to the O atoms of L1. The observed distances between the diagonally placed O atoms in L1 are 6.2Å and 4.7Å, but for the corresponding diagonally placed S atoms in L2, these distances are increased to 7.4Å and 5.7Å, respectively. The distances between the macrocyclic Ns in both L1 are L2 are observed to be 7.9Å. This indicate that due to the differences in the dimensions of the O and S atoms, the ring cavity is expanded in case of L2, even though the position of the ring Ns remains practically unchanged.
The frontier molecular orbital analysis of these ligands show that their HOMOs are majorly localised at the -COO region of the dipicolinate pendant arms [Fig.3]. This indicates that the bonding with metal ions will be predominantly via these centres[17]. The energy separation between the HOMO and the LUMO being a marker of reactivity indicates that the L2 ligand is more reactive than the L1 [Fig.3]. The manifestation of the difference in reactivities in the bonding will be studied in the subsequent sections.
(ii) Geometrical parameters of the metal complexes of L1 and L2

The optimised structures of the metal-ligand complexes are presented in Fig. 4. In all the complexes, the metal ion is encapsulated by the dipicolinate arms of the ligand and it doesn’t sit directly in the cavity of the aza-macrocyclic unit. It is placed above the plane of the aza-macrocyclic unit, toward the COO\(^{-}\) groups. The stable \((\delta\lambda\delta)(\delta\lambda\delta)\) conformers were taken as the starting structures for optimisation[16, 17]. Interestingly, even for the L2 complexes, the \((\delta\lambda\delta)(\delta\lambda\delta)\) helicity of the dipicolinate arms was retained after optimisation. This implies that the cavity orientation is not much altered, barring the spatial disposition of the donor O and S atoms. Two sets of equivalent O/S donors of the aza-macrocycle were identified. Two of them were close to the metal and two were away [Fig. 4]. From Table 1 it is seen that the M-OCO and M-N(Py) bond distances did not change substantially upon the replacement of the aza-crown oxygens by sulphurs, but there was observable change in the M-S/O and M-N(Ring) bond lengths. The calculated bond parameters are well in agreement with ones previously reported[16], rendering our level of theory benchmarked. Further studies are carried out in order to understand the bonding features of the Am(III) and Cm(III) complexes of L1 and L2.
Table 1. Structural parameters of the Am/Cm complexes of L1 and L2, …(…) calculated and literature[16] values respectively

<table>
<thead>
<tr>
<th>System</th>
<th>M-O1/S1 (Å)</th>
<th>M-O2/S2 (Å)</th>
<th>M-OCO (Å)</th>
<th>M-N(py) (Å)</th>
<th>M-N(ring) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AmL1</td>
<td>2.81(2.78)</td>
<td>2.90(2.88)</td>
<td>2.27(2.28)</td>
<td>2.62(2.64)</td>
<td>3.04(3.04)</td>
</tr>
<tr>
<td>CmL1</td>
<td>2.77(2.76)</td>
<td>2.94(2.90)</td>
<td>2.28(2.29)</td>
<td>2.60(2.63)</td>
<td>3.01(3.01)</td>
</tr>
<tr>
<td>AmL2</td>
<td>3.09</td>
<td>3.09</td>
<td>2.27</td>
<td>2.62</td>
<td>3.36</td>
</tr>
<tr>
<td>CmL2</td>
<td>3.10</td>
<td>3.11</td>
<td>2.27</td>
<td>2.60</td>
<td>3.29</td>
</tr>
</tbody>
</table>

(iii) FMO Analysis of the Complexes

The FMOs of the complexes along with the metallic contributions and energy gaps between them are presented in Fig 5. The energy gaps between the SOMO and LUMO of the complexes are in the order CmL1>CmL2>AmL2>AmL1. This implies that in general the Cm(III) forms more stable complexes with the ligands in comparison to Am(III). However, the Cm ions form more stable complex with L1 ligands, but Am ions form more stable complex with L2. The HOMO-LUMO gaps of the L1 and L2 ligands are observed to be 4.20 eV and 4.10 eV respectively. Similar gap is observed in their respective Cm complexes. Interestingly, the trend is reversed for the Am complexes and an additional stabilization, exceeding the ligand energy gap, is observed for the AmL2 complex in comparison to AmL1. This additional interaction may be attributed to the significantly
higher metallic contribution in the FMOs that is observed in the Am complexes. Participation of the macrocyclic S’s is also seen in the L2 complexes. But for the L1 complexes the localisation of electrons is observed only at the carboxylate groups. The extent of charge transfer from the donor centres of the ligands to metal centres is expected to provide an insightful information about the donor-acceptor properties of the system, hence was studied next.

![Frontier MOs of the Am/Cm-L1/L2 complexes](image)

**Fig. 5. Frontier MOs of the Am/Cm-L1/L2 complexes**

**(iii) Partial charge analysis in the Complexes**

The natural and AIM charges on the complexes and ligands were calculated and presented in [Table-S2]. The ligand to metal charge transfer (LMCT) was calculated by subtracting the present charge on the metal ion, obtained from both the methods of calculation from its original charge of ‘+3’. A correlation plot of the LMCT obtained by NPA and AIM is presented in [Fig 6]. Significantly higher LMCT is observed for Am complexes than Cm. Also, the L2 ligands are seen to contribute more to LMCT. This may be attributed to the higher polarizability, hence electron donation capacity of S over O. Also the lower LMCT to Cm, even though it has a higher charge to radius ratio than Am, maybe attributed to its initial half-filled f-configuration. Similar observation was also noted in the FMO analyses of the complexes, where the metallic contribution of Cm to the SOMO/LUMO is significantly lower than that of Am. A topological analysis of the complexes is important to understand the
disposition of electron clouds along the bonds. The electron densities at the bond critical points and the derived quantities, provide important information about the covalent contribution in the bonds. Hence QTAIM analysis was carried out for understanding the nature of the bonds in these complexes.

(iv) QTAIM Analysis

The metrics of the QTAIM study are helpful towards understanding the degree of covalency in a bond, as a function of the electron density present at the bond critical point (BCP). The variation of this electron density at the BCPs was found to be marginal and values are presented in Table-S3. As a rule of thumb, a negative $\nabla^2 \rho'$ indicates a covalent bond. Alongside, a positive $\nabla^2 \rho'$ and negative H(r) at BCP indicate partial covalency. To identify the nature of the metal-donor bonds, the above mentioned parameters were calculated and presented in Table 2.

Table 2: (a) $\nabla^2 \rho'$ and (b) H(r) at BCP for all M-L bonds.

<table>
<thead>
<tr>
<th>System</th>
<th>M-O/S1</th>
<th>M-O/S2</th>
<th>M-O/S3</th>
<th>M-O/S4</th>
<th>M-COO1</th>
<th>M-COO2</th>
<th>M-PyN1</th>
<th>M-PyN2</th>
<th>M-RingN1</th>
<th>M-RingN2</th>
</tr>
</thead>
<tbody>
<tr>
<td>AmL1</td>
<td>0.09</td>
<td>0.07</td>
<td>0.09</td>
<td>0.07</td>
<td>0.31</td>
<td>0.31</td>
<td>0.14</td>
<td>0.14</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>CmL1</td>
<td>0.10</td>
<td>0.07</td>
<td>0.10</td>
<td>0.07</td>
<td>0.31</td>
<td>0.31</td>
<td>0.14</td>
<td>0.14</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>AmL2</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
<td>0.32</td>
<td>0.32</td>
<td>0.14</td>
<td>0.14</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>CmL2</td>
<td>0.06</td>
<td>0.07</td>
<td>0.06</td>
<td>0.07</td>
<td>0.32</td>
<td>0.32</td>
<td>0.14</td>
<td>0.14</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>
The data from Table 2 indicate that the M-OCO and M-PyN bonds have the highest covalent nature in all the complexes. Interestingly, the O/S donors of the aza-macrocycle have different bonding interactions. The M-S bonds in the ML2 systems have partial covalency unlike the M-O bonds in ML1 system. And the extent of covalency is higher for the Am-S bonds than the Cm-S bonds as the H(r) values are more negative for the Am-S bonds. This observation is in line with the bond indices data encompassing the and the delocalisation indices and the Wiberg bond indices in Table-S4. After elucidation of the nature of the metal-donor bonds from the QTAIM analysis, a picture of specific orbital interactions corresponding to the covalency was intriguing to understand.

(v) Natural Electronic Configuration of the metal in the complexes

The number of electrons over and above the initial electronic configuration of the Am or Cm centres in the complexes were obtained from the robust natural population analysis. A bar graph showing these comparative data is presented in Fig. 7.

```
<table>
<thead>
<tr>
<th>System</th>
<th>M-O/S1</th>
<th>M-O/S2</th>
<th>M-O/S3</th>
<th>M-O/S4</th>
<th>M-COO1</th>
<th>M-COO2</th>
<th>M-PyN1</th>
<th>M-PyN2</th>
<th>M-RingN1</th>
<th>M-RingN2</th>
</tr>
</thead>
<tbody>
<tr>
<td>AmL1</td>
<td>2.508</td>
<td>2.293</td>
<td>2.508</td>
<td>2.293</td>
<td>-17.506</td>
<td>-17.507</td>
<td>-3.681</td>
<td>-3.678</td>
<td>1.001</td>
<td>1.001</td>
</tr>
<tr>
<td>CmL1</td>
<td>2.618</td>
<td>2.295</td>
<td>2.618</td>
<td>2.295</td>
<td>-15.517</td>
<td>-15.514</td>
<td>-4.112</td>
<td>-4.111</td>
<td>0.935</td>
<td>0.934</td>
</tr>
<tr>
<td>AmL2</td>
<td>-1.651</td>
<td>-1.208</td>
<td>-1.208</td>
<td>-1.651</td>
<td>-17.649</td>
<td>-17.648</td>
<td>-3.527</td>
<td>-3.527</td>
<td>1.234</td>
<td>1.233</td>
</tr>
<tr>
<td>CmL2</td>
<td>-1.219</td>
<td>-1.015</td>
<td>-1.219</td>
<td>-1.014</td>
<td>-15.956</td>
<td>-15.955</td>
<td>-4.057</td>
<td>-4.056</td>
<td>1.293</td>
<td>1.293</td>
</tr>
</tbody>
</table>
```

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Fig 7. Plot of excess number of electrons in metal orbitals in the complexes.
```
S donors of L2. Donation of electrons to the 5f orbitals of Am and Cm is also observed. The number of f-electrons on the metal center in the complex beyond its initial f-configuration (f-excess), is higher for Am-complexes than Cm-complexes which is in line with the observations from LMCT and FMO analyses. Higher number of f-excess electrons in Am center in comparison to the Cm center in their complexes with variety of N,O donor based ligands has also been reported earlier[14]. This indicates that Am(III) is eager to accept more electrons to achieve the half-filled f-configuration, unlike Cm(III), where the initial half-filled f configuration of the 5f orbitals resists the further acceptance of electrons[43]. As the extent of covalent bonding is established to be higher in the L2 complexes than that in the L1 complexes, and the only difference among the ligands L1 and L2 lies in the macrocyclic O and S donors, the orbital composition of the metal centres in the natural bond orbitals of Am-S and Cm-S bonds were studied.

(vi) Natural Bond Orbital analysis of the M-S bonds in the L2 complexes

The orbital composition of the metal center in the M-S bonds of the ML2 complexes is presented in Table 3.

<table>
<thead>
<tr>
<th>System</th>
<th>Bond</th>
<th>Orbital Composition of M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M-S1</td>
<td>s(22.90%)p(0.34%)d(65.79%)f(10.98%)</td>
</tr>
<tr>
<td>AmL2</td>
<td>M-S2</td>
<td>s(18.12%)p(0.50%)d(48.44%)f(32.95%)</td>
</tr>
<tr>
<td></td>
<td>M-S3</td>
<td>s(18.12%)p(0.50%)d(48.44%)f(32.95%)</td>
</tr>
<tr>
<td></td>
<td>M-S4</td>
<td>s(22.90%)p(0.34%)d(65.79%)f(10.98%)</td>
</tr>
<tr>
<td>CmL2</td>
<td>M-S1</td>
<td>s(20.49%)p(0.44%)d(78.86%)f(0.22%)</td>
</tr>
<tr>
<td></td>
<td>M-S2</td>
<td>s(24.23%)p(0.48%)d(75.09%)f(0.20%)</td>
</tr>
<tr>
<td></td>
<td>M-S3</td>
<td>s(24.23%)p(0.48%)d(75.09%)f(0.20%)</td>
</tr>
<tr>
<td></td>
<td>M-S4</td>
<td>s(20.49%)p(0.44%)d(78.86%)f(0.22%)</td>
</tr>
</tbody>
</table>

As was observed in the natural electronic configurations of the metal centres in whole complex as well as the M-S bonds have the similar trend, i.e., predominance of 6d orbital participation over 5f. However, the 5f participation is much restricted in case of Cm than Am. Similar observation is also noted from the density of states plot in Fig-S1. After probing the orbital participation in the bonding, it was imperative to understand the energetic contribution of these orbital interactions in the bonding energies, which was hence calculated by energy decomposition analysis.

(vii) Energy Decomposition Analysis (EDA-NOCV)
In the energy decomposition analysis, the bonding energy between the trivalent metal ion and the ligand is decomposed into attractive electrostatic and orbital components as well as repulsive Pauli component. The relative orbital contribution is a marker of the extent of covalent bonding in the systems. In the data from Table 4 we see that the predominant bonding is via the electrostatic interaction and the bonding energies are more negative for the Cm complexes, than the Am complexes. Also, the L1 complexes have more negative bonding energies than L2 complexes. The L2 complexes are observed to have higher Pauli repulsion amongst its electrons than L1 complexes possibly due to the higher extent of ligand to metal charge transfer in them, especially by the less electronegative sulphur donors. Amongst the Am and Cm complexes, the Am complexes have higher Pauli repulsion due to the similar reason.

<table>
<thead>
<tr>
<th>System</th>
<th>Bonding Energy</th>
<th>∆E_pauli (kcal/mol)</th>
<th>∆E_orb (kcal/mol)</th>
<th>∆E_elstat (kcal/mol)</th>
<th>∆E_orb %</th>
<th>∆E_elstat %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AmL1</td>
<td>-1070.43</td>
<td>203.29</td>
<td>-433.44</td>
<td>-840.3</td>
<td>34.0</td>
<td>66.0</td>
</tr>
<tr>
<td>CmL1</td>
<td>-1071.06</td>
<td>194.09</td>
<td>-427.15</td>
<td>-838.01</td>
<td>33.8</td>
<td>66.2</td>
</tr>
<tr>
<td>AmL2</td>
<td>-1039.99</td>
<td>225.02</td>
<td>-463.08</td>
<td>-801.91</td>
<td>36.6</td>
<td>63.4</td>
</tr>
<tr>
<td>CmL2</td>
<td>-1043.48</td>
<td>212.77</td>
<td>-456.11</td>
<td>-800.12</td>
<td>36.3</td>
<td>63.7</td>
</tr>
</tbody>
</table>

However, the orbital interaction energies and their % contributions to the attractive terms have higher magnitude for the Am complexes than Cm complexes. Amongst the L1 and L2 complexes, the latter have higher value of these energies. Hence, the bonding trends match the energetic contributions. Similar trend in the energy decomposition analysis was also observed for transplutonium complexes of ligands involving O and S atoms viz. Cyanex 301, 302 and 272[15]. Now for a visualisation of the electron flow channels contributing to the ∆E_orb, the NOCV analysis was carried out. The highest contributing channels are plotted in Table 5.

Table 5. NOCV Deformation density channels contributing predominantly to the ∆E_orb.
In all of the deformation channels, predominant donation of electron from the carboxylate group to the metal ions is reflected. Lowering of electron density is also observed for the pyridine N’s, reflecting their participation in bonding too, as was seen in QTAIM analysis. Signature of metal d-orbitals is visible on the metal ions, indicating it to be the major orbital for accepting electrons, as was also seen in the previous sections. Interestingly, significant electron donation from the macrocyclic S donors is seen in the L2 systems, but the corresponding O’s in the L1 complexes are not observed to participate in that extent. Finally, the manifestation of the bonding analysis into the experimentally observable thermodynamic quantities was studied.

(viii) Thermodynamic Study

The trivalent Am and Cm ions reportedly exist in nine coordinated aqua complexes when present in water[44, 45]. Hence, the initial configuration of the metal ions was explicitly modelled as these complexes and implicit accounting of water as the solvent medium was carried out by implementing CPCM approach[31]. Equation (1) was used to study the thermodynamics of the complexation of the metal ion with the ligand.

$$[\text{M(H}_2\text{O)}_9]^3^+ (\text{aq.}) + \text{L}^2^- (\text{aq.}) = [\text{ML}]^+ (\text{aq.}) + (\text{H}_2\text{O})_9(\text{aq.}); \text{M} = \text{Am or Cm}$$

..... (Equation 1)

The Gibbs free energies of the complexes at 298.15K are presented in Table 6.

<table>
<thead>
<tr>
<th>Systems</th>
<th>$\Delta G$ (kcal/mol)</th>
<th>$\Delta \Delta G_{\text{Am/Cm}}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AmL1</td>
<td>-30.57</td>
<td>-1.14</td>
</tr>
<tr>
<td>CmL1</td>
<td>-29.43</td>
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<tr>
<td>AmL2</td>
<td>-37.04</td>
<td>-2.97</td>
</tr>
<tr>
<td>CmL2</td>
<td>-34.07</td>
<td></td>
</tr>
</tbody>
</table>

It is observed that the L2 complexes have more negative $\Delta G$ values than the L1 complexes, rendering the former more suitable for extraction of both the metal ions. However, for separating the metal ions, difference in their $\Delta G$ values must be present, so that a selectivity is achieved. Both the ligands show more negative $\Delta G$ for Am ion, rendering them Am selective. This finding affirms our modelling of the thermodynamic reaction, as L1 is experimentally established to be Am selective[16]. However, to quantify the extent of selectivity, the $\Delta \Delta G$ values, i.e., the difference between $\Delta G_{\text{Am}}$ and $\Delta G_{\text{Cm}}$ are calculated. Considering this, better Am-selectivity is noted for L2 ligand.

Conclusions:

This study provides several insights into the bonding features and their manifestation in the energetics upon complexation of the chemically similar trivalent Am and Cm ions with the donor center modulated aza-
macroyclic based ligands L1 and L2. Predominant mode of metal-ligand bonding is identified to be electrostatic in nature and is via the carboxylate moiety in the dipicolinate pendant arms of both the ligands. The subtle differences in the bonding is brought about by the covalent interaction of the metal and the aza-macroyclic O and S donors. The electron donation from the ligand is mostly accepted in the metal 6d orbitals and minimally to the 5f orbitals. The extent of 6d orbital interactions is nearly same for both Am(III) and Cm(III) ions, but the magnitude is much higher for the L2 complexes. The f-orbital participation plays a crucial role in bringing about the subtle difference in the bonding between Am(III) and Cm(III) ions with the ligands. The trivalent Cm ion with half-filled initial f^{7} configuration shows resistance in participating in bonding. Whereas, the Am(III) ions having f^{6} configuration are hungry for f-electrons to achieve the stable half-filled configuration. Upon studying the energetics, it was elucidated that both L1 and L2 ligands are Am selective, i.e., Am complexes have more negative Gibbs free energy values than Cm complexes. But the extraction capacity and selectivity is higher for the L2 ligand. The Am selectivity can be attributed to the significant covalent interaction of S donors which have better electron donating capacity (than O) with the f-electron deficient Am(III) ion. Even though Am(III) ion is only marginally softer than Cm(III) ion, the impact of softer donor centre (S) is observed to be significant in increasing the selectivity between the ions, similar to that observed in lanthanide-actinide separations. This study is expected to impact the designing of ligands for the separation of these two minor actinides.

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There is no competing interest to declare.

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- **Saparya Chattaraj**: Data curation, Formal Analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft
• **Arunasis Bhattacharyya**: Conceptualization, Investigation, Methodology, Resources, Supervision, Writing – review & editing

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**Availability of data and materials:**

Can be provided as and when required.

**References:**


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