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Computational chemical analysis of Eu(III) and Am(III) complexes with pnictogen-donor ligands using DFT calculations†

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We demonstrated density functional calculations of Eu(III) and Am(III) complexes with pnictogen-donor (X) ligands, (CH₃)₂X–CH₂–CH₂–X(CH₃)₂ (X = N, P, As and Sb). We investigated the optimized structures of the complexes and the Gibbs energy differences in the complex formation reactions. The results indicated that the N- and P-donor ligands exhibit Am(III) ion selectivity over Eu(III) ions; especially, the P-donor ligand showed the highest selectivity. The tendency of the Am(III)/Eu(III) selectivity by the pnictogen-donor ligands was found to be comparable to that of the soft acid classification in the hard and soft acids and bases rule. Mulliken's spin population analysis indicated that the bonding properties between the metal ion and the pnictogen atoms correlated with the Am(III)/Eu(III) selectivity. In particular, the participation of f-orbital electrons of the metal ion in the covalency was indicated to play an important role in the selectivity.

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Introduction

Separation of minor actinides (MA = Np, Am and Cm) from lanthanides (Ln) is important for the safe disposal of high-level radioactive liquid waste. Because MA nuclides have extremely long half-life periods and high radiotoxicity, shortening the half-lives by transmutation after selective separation of MA, *i.e.* the partitioning and transmutation strategy, has been required as a rational method of disposal of spent nuclear fuel. However, selective separation of MA from Ln is challenging, because the chemical properties of MA ions, such as oxidation state, geometrical structure, stability in solution, and so on, are similar to those of Ln ions.¹

Solvent extraction is one of the most useful methods for the separation of MA(III) ions from Ln(III) ions. The selectivity of MA(III) ions over Ln(III) ions has been indicated to depend on the kind of the donor atom of the ligands used in solvent extraction. For example, O-donor ligands tend to separate Ln(III) ions from MA(III) ions, but S-donor ligands tend to sep-

arate MA(III) ions from Ln(III) ions.² The selectivity has often been explained using the hard and soft acids and bases (HSAB) rule,³ namely, the hard property of the O-donor ligand compared to that of the S-donor ligand or the soft property of the S-donor ligand compared to that of the O-donor ligand. Relativistic quantum chemical calculation using the Dirac–Hartree–Fock Hamiltonian indicated that an Am(III) ion has more diffused valence d- and f-orbitals than a Eu(III) ion.⁴ This result implied the softer property of Am(III) ions compared to that of Eu(III) ions and supported the selective separation of MA(III) ions over Ln(III) ions using S-donor ligands.

N-Donor ligands have been investigated as an alternative to S-donor ligands from the viewpoints of high tolerance to acids, ease of synthesis, soft base property and chemical stability.⁵ When focusing on the HSAB tendency of pnictogen elements, which are N, P, As and Sb, N-donor ligands form stable complexes with hard metal ions compared to P-, As- and Sb-donor ligands, whereas P-, As- and Sb-donor ligands form more stable complexes with soft metal ions compared to N-donor ligands.³ This implies that P-, As- and Sb-donor ligands have the higher selectivity for MA(III) ions over Ln(III) ions than N-donor ligands. A recent report indicated that bis(diphenylphosphino)alkanes as P-donor ligands show the selectivity of Am(III) ions over Eu(III) ions.⁶ However, there are no systematic experimental and theoretical studies of the MA(III)/Ln(III) selectivity by pnictogen-donor ligands.

Density functional theory (DFT) calculations have been applied successfully to understand the coordination geometry, stability and chemical bonding,^{7–10} leading to the elucidation

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† Electronic supplementary information (ESI) available: Total energies and Gibbs correction energies for all compounds and Cartesian coordinates of calculated geometries and MO energy data with partial density of states of metal ions and overlap population between the metal ion and the donor atoms in the valence region for [M(DMXE)(H₂O)₆]³⁺. See DOI: 10.1039/c8dt01973h

of the separation mechanism between MA(III) ions and Ln(III) ions.¹¹ Our previous studies showed that Eu(III) ions favor the O-donor ligands and Am(III) ions favor the N- and S-donor ligands in terms of the bonding properties using scalar-relativistic DFT calculations and suggested that the differences of f-orbitals between Eu(III) and Am(III) ions play an important role in the selectivity.^{12–14} Our recent study also indicated that the relative complexation reaction energies between Am(III) and Eu(III) ions with chalcogen-donor ligands are comparable to the tendency of the soft acid classification for chalcogen elements in the HSAB rule by correlating the Am(III)/Eu(III) selectivity by chalcogen-donor ligands with the covalency in the coordination bonds between the metal ion and chalcogen-donor atoms.¹⁵

This work aims to compare systematically the coordination bonding between Am(III)/Eu(III) ions and the pnictogen-donor ligands in each complex by means of DFT calculations and the electron population analysis. In this paper, we set the same structure for complexes, $[M(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$ ($M = \text{Eu}$ and Am ; $\text{DMXE} = (\text{CH}_3)_2\text{X}-\text{CH}_2-\text{CH}_2-\text{X}(\text{CH}_3)_2$ ($\text{X} = \text{N}, \text{P}, \text{As}$ and Sb)), in order to discuss systematically the Am(III)/Eu(III) complexes with pnictogen-donor ligands, as defined in Fig. 1. We focus on three points: (i) which donor ligands are suitable to separate Am(III) ions from Eu(III) ions among pnictogen-donor systems, (ii) what is the origin of Am(III)/Eu(III) selectivity by pnictogen-donor ligands and (iii) whether there are some correlations between DFT results and the HSAB rule, or not. It is expected that this study contributes to the understanding of the fundamental nature of chemical bonding in f-block metal complexes and to the design of novel extraction reagents with higher separation efficiency between MA(III) ions and Ln(III) ions.

Computational details

All calculated complexes, $[M(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$, were modeled by referring to the coordination sphere of the single crystal structure, $[\text{U}(\text{DMPE})(\text{DMBPY})\text{Cl}_4]$ ($\text{DMPE} = 1,2$ -bis(dimethylphosphino)ethane; $\text{DMBPY} = 4,4'$ -dimethyl-2,2'-bipyridine).¹⁶ The initial structures for geometry optimization calculation were created by changing the four chlorine atoms and the two nitrogen atoms of a DMBPY ligand to six oxygen atoms of hydrated water and the two phosphorus atoms of a DMPE ligand to each two nitrogen, arsenic and antimony atoms. It should be noted that the consideration of only hexa-hydrated

models is based on two reasons. These are to assure the reproducibility for modeling the complex, $[\text{M}(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$, and due to difficulty obtaining the hepta-hydrated complex, $[\text{M}(\text{DMXE})(\text{H}_2\text{O})_7]^{3+}$. We considered the reaction scheme for the complex formation of $[\text{M}(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$ as shown in eqn (1).



We considered here the hydration complexes of Eu(III) and Am(III) as $[\text{M}(\text{H}_2\text{O})_9]^{3+}$, because the most stable oxidation state of Eu and Am in solution is generally the trivalent¹⁷ state and the hydration numbers of the hydrated complexes were reported as 8.71 or 8.85 for Eu(III) species^{18,19} and 9.00 for Am(III) species.²⁰

The Gibbs energy difference (ΔG) in the complex formation reaction defined as eqn (1) was estimated by using eqn (2). G_{final} and G_{initial} are the sum of the standard Gibbs energies (298 K, 1.0 atm) of the products and reactants, respectively, and the Gibbs energies were calculated by using eqn (3)–(6).

$$\Delta G = G_{\text{final}} - G_{\text{initial}} \quad (2)$$

$$G = E^{\text{total}} + G^{\text{corr}} \quad (3)$$

$$G^{\text{corr}} = H^{\text{corr}} - TS \quad (4)$$

$$H^{\text{corr}} = E^{\text{vibration}} + E^{\text{rotation}} + E^{\text{translation}} + k_{\text{B}}T \quad (5)$$

$$S = S^{\text{spin}} + S^{\text{vibration}} + S^{\text{rotation}} + S^{\text{translation}} \quad (6)$$

The E^{total} term was obtained by single point energy calculation. The G^{corr} term is the thermal Gibbs correction term and this term is composed of a thermal enthalpy correction (H^{corr}) term and an entropy (S) term. The H^{corr} term is the sum of vibrational, rotational, and translational energies, which are $E^{\text{vibration}}$, E^{rotation} , and $E^{\text{translation}}$, respectively, and $k_{\text{B}}T$. k_{B} is the Boltzmann constant and T is the temperature. The S term is the sum of spin, vibrational, rotational, and translational contributions to entropy. It should be noted that the contributions to entropy in this calculation did not consider the conformation, dissociation and COSMO solvation effects as several publications reported.^{21,22} The vibrational contributions to the Gibbs energy were calculated as the quasi-harmonic approximation, which is the same as the usual harmonic oscillator approximation, except that normal vibrational frequencies less than 60 cm^{-1} were increased to 60 cm^{-1} to correct for the well-known breakdown of the harmonic oscillator model for the free energies of low-frequency vibrational modes.^{23,24} The rotational contributions to the Gibbs energy were approximated as the rigid rotator, in which the symmetric number was set to 1 for $[\text{M}(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$ and 3 for $[\text{M}(\text{H}_2\text{O})_9]^{3+}$.

All DFT calculations were performed by using the program ORCA 3.0.0.²⁵ A scalar-relativistic effect was considered using a relativistic effective core potential (RECP) method^{26–28} and zeroth-order regular approximation (ZORA) Hamiltonian^{29,30} with segmented all-electron relativistically contracted (SARC) basis sets.^{31–33} The spin-orbit coupling effect was estimated by the Breit–Pauli perturbative method.³⁴ We used the scalar

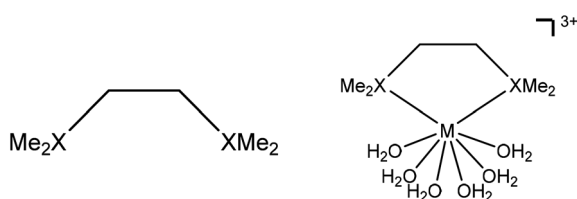


Fig. 1 Chemical formulas of the DMXE ligand (left) and the complex (right), $[\text{M}(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$ ($M = \text{Eu}, \text{Am}$; $\text{X} = \text{N}, \text{P}, \text{As}$ and Sb).

ZORA Hamiltonian with SARC basis sets for all the DFT calculations except for only geometry optimization of Eu(III) complexes. In the geometry optimization of Eu(III) complexes, a 52-electron-core pseudopotential with the (8s7p6d)/[6s5p5d] basis set for the Eu atom,²⁶ a 28-electron-core pseudopotential²⁷ with the (21s20p9d1f)/[5s4p3d1f] basis set²⁸ for the Sb atom, which was collected by using the Basis Set Exchange (BSE) software and the EMSL Basis Set Library,^{35,36} and TZVP basis sets for the other atoms³⁷ were employed due to the difficulty in obtaining the converged geometries for Eu(III) complexes when using the ZORA method with SARC basis sets. Single point energy calculations of Eu(III) complexes were performed using the all-electron ZORA Hamiltonian with SARC basis sets with (23s16p12d6f)/[18s12p9d3f] contraction for the Eu atom³¹ and TZVP-SARC basis sets for the other atoms³³ at the optimized geometries. The equilibrium geometries of Am(III) complexes were obtained by using a SARC basis set with (29s20p16d12f)/[21s13p10d7f] contraction for the Am atom³² and an SVP-SARC basis set for the other atoms.³³ Single point energy calculations for Am(III) complexes were performed with SARC basis sets for Am³² atoms and TZVP-SARC basis sets for the other atoms.³³ The BP86^{38,39} functional was employed for geometry optimization without any symmetrical constraints. Normal vibrational mode calculations were carried out at optimized geometries to check the local minima under the same conditions as geometry optimization and to obtain the vibrational contribution to the thermal correction. We observed that their geometries were located at a local minimum where the normal vibrational modes have no imaginary frequencies. The B2PLYP⁴⁰ functional was used for single point energy calculations considering the solvation effect of water by a conductor-like screening model (COSMO),⁴¹ in which the COSMO radii were set to 1.90 and 1.99 Å for Eu and Am atoms, respectively.^{42,43} Resolution of the identity (RI) approximations^{44,45} were employed to reduce the computational cost during self-consistent field (SCF) calculations. Open-shell compounds, such as Eu(III) and Am(III) complexes, which have a spin septet state as the electronic ground state, were calculated using an unrestricted Kohn–Sham procedure. Spin contamination was confirmed to be low in all the calculations, because the deviation of the expectation value, $\langle S^2 \rangle$, to the ideal value, $S(S + 1)$, was 1.2% for the

maximum value, which was negligibly small. The conditions of the integral grid numbers and threshold values for convergence in SCF calculations were set to the same criteria as in our previous publications.¹² Three-dimensional descriptions of the optimized structures and molecular orbital (MO) surfaces, generated by orca_plot.exe at 5.0×10^{-5} electron per bohr³, were visualized by using the program VESTA ver. 3.1.8.⁴⁶ Natural atomic spin population,^{47,48} which was obtained by NBO 6.0,⁴⁹ Mulliken's atomic spin population⁵⁰ and MO overlap population⁵¹ analyses based on single point energy calculations were performed in order to discuss the correlation of the electronic properties between the metal ion and the donor atoms in the complexes, $[M(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$.

Results and discussion

Equilibrium structures of $[M(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$

All the complexes, $[M(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$, were obtained with local minimum structures and had the square antiprism geometry in the MX_2O_6 coordination sphere as shown in Fig. 2, and the Cartesian coordinates of all complexes are available in the ESI† in an xyz file format in angstrom unit. Interestingly, the chelating style of the DMXE ligand to the metal ion was indicated to be slightly different between $X = \text{N}$ and the others, although the same starting coordinates were employed for optimization. In the case of the complex with $X = \text{N}$, the two N-donor atoms coordinate to the metal ion as a bridge between the two square planes. In the case of the complexes with $X = \text{P}$, As and Sb, the two X-donor atoms are configured in the same square plane. This difference in the chelating style might be caused by the differences in the distances between the square planes and/or the distortion of the ligands when forming the coordination bonds; however the details are still unclear. Here we assumed that this difference in the coordination geometry between N-donor complexes and the other complexes has no great effects on the Am(III)/Eu(III) selectivity, because there was an indication that the Am(III)/Eu(III) selectivity and the bonding properties do not depend on the difference in the conformers of the complexes as found in the complexes with phosphinic acid, dithiophosphinic acid and diglycolamide ligands.^{13,14} Table 1 shows the calculated bond

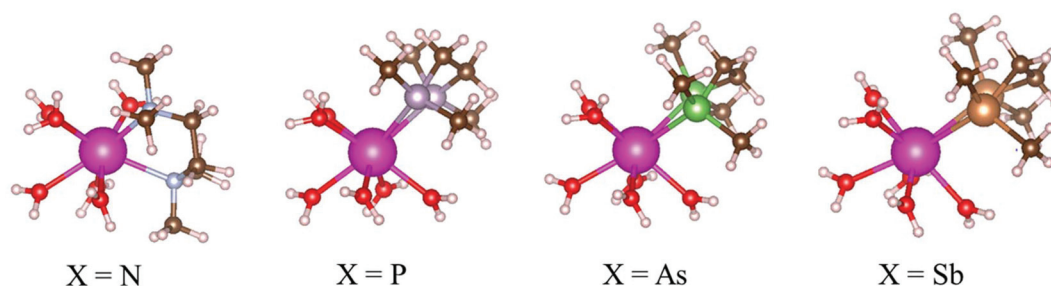


Fig. 2 Ball-and-stick illustrations of optimized complexes, $[M(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$, in which pink, blue, purple, green, orange, brown, red, and white spheres show metal, N, P, As, Sb, C, O, and H elements, respectively.

Table 1 Averaged metal–ligand bond lengths in the optimized Eu(III) and Am(III) complexes, $r_{\text{ave}}(\text{M}-\text{X})$, and the difference between $r_{\text{ave}}(\text{M}-\text{X})$ and the sum of $r_{\text{ion}}(\text{M})^{\text{a}}$ and $r_{\text{cov}}(\text{X})^{\text{b}}$, $\Delta r = r_{\text{ave}}(\text{M}-\text{X}) - \{r_{\text{ion}}(\text{M}) + r_{\text{cov}}(\text{X})\}$

Complex	$r_{\text{ave}}(\text{M}-\text{X})/\text{\AA}$		$\Delta r/\text{\AA}$	
	M = Eu	M = Am	M = Eu	M = Am
X = N	2.625	2.658	0.85	0.86
X = P	3.098	3.152	0.92	0.95
X = As	3.188	3.260	0.91	0.96
X = Sb	3.413	3.550	0.95	1.06

^a Shannon's ionic radii from ref. 52. ^b Pyykkö's covalent radii from ref. 53.

lengths between the metal ions and the donor atoms, $r_{\text{ave}}(\text{M}-\text{X})$, of $[\text{M}(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$ (M = Eu and Am). When comparing the r_{ave} values between Eu–X and Am–X, we can see that Am(III) complexes have longer bond lengths than Eu(III) complexes for all systems and the difference between $r_{\text{ave}}(\text{Eu}-\text{X})$ and $r_{\text{ave}}(\text{Am}-\text{X})$ increased in the order of X = N, P, As and Sb. In Table 1, we also show the Δr values, which are the differences between $r_{\text{ave}}(\text{M}-\text{X})$ and the sum of Shannon's ionic radii, $r_{\text{ion}}(\text{M})$,⁵² and Pyykkö's covalent radii, $r_{\text{cov}}(\text{X})$,⁵³ to compare the bonding properties between 4f- and 5f-block metal complexes. The values of $r_{\text{cov}}(\text{X})$ for single-bonds were defined as 0.71, 1.11, 1.21 and 1.40 Å for X = N, P, As and Sb, respectively.⁵³ The values of $r_{\text{ion}}(\text{M})$ employed were 1.07 and 1.09 Å for Eu(III) and Am(III) ions, respectively.⁵² The Δr values of X = N were smaller than those of X = P, As and Sb in both of the M = Eu and Am systems. This result implied roughly the difference in hardness and softness among the coordination bonds in the complexes. In other words, there was an indication that the N-donor ligand, as a harder base, forms stronger coordination bonds with Eu(III) and Am(III) ions, as hard acids, compared with the P, As and Sb-donor ligands, which are softer bases. This result was qualitatively comparable to the discussion on the HSAB rule and indicated the ionic bonding character of the coordination bonds in the Eu(III) and Am(III) complexes.

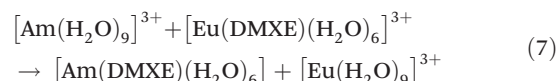
Complexation energies from $[\text{M}(\text{H}_2\text{O})_9]^{3+}$ to $[\text{M}(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$

Table 2 shows the ΔG values of each complex, based on the complexation reaction as shown in eqn (1) and the numerical data of E^{tot} and G^{corr} for all compounds are available in Table S1.† This result indicated that the ΔG values increased

Table 2 Calculated ΔG values for Eu(III) and Am(III) complexes defined as eqn (1)

Reactions	$\Delta G(\text{M})/\text{kJ mol}^{-1}$		$\Delta G(\text{Am}) - \Delta G(\text{Eu})/\text{kJ mol}^{-1}$
	M = Eu	M = Am	
X = N	−34.79	−35.85	−1.06
X = P	−8.72	−11.55	−2.83
X = As	20.01	19.83	−0.18
X = Sb	51.68	55.81	4.12

in the order of X = N, P, As and Sb for both Eu(III) and Am(III) systems. This means that the stability of $[\text{M}(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$ relative to $[\text{M}(\text{H}_2\text{O})_9]^{3+}$ decreases in the order of X = N, P, As and Sb. This tendency is consistent with the hard acid classification.³ This might be caused by the ionic bonding character as shown in the above discussion of the metal–ligand bond lengths. We also estimated the difference in the ΔG values between Eu(III) and Am(III) systems and the values of $\Delta G(\text{Am}) - \Delta G(\text{Eu})$ are shown in Table 2. These values can be considered as the Gibbs energy difference in eqn (7) and have been employed as indicators to predict Am(III)/Eu(III) selectivity.^{54–57}



The obtained values were indicated to be negative for the complexes with X = N, P and As and the tendency of the Am(III)/Eu(III) selectivity was P > N > As > Sb, which corresponds to the soft acid classification.³ Interestingly, the P-donor ligand is expected to show the best selectivity of Am(III) ions over Eu(III) ions in pnictogen-donor ligands. The result of the Am(III) selectivity over Eu(III) by the P-donor ligand was supported by a previous experimental report.⁶ The tendencies in hard acid classification for the complexation reaction and soft acid classification for the Am(III)/Eu(III) selectivity were confirmed to be the same in the complexation reaction using $[\text{M}(\text{H}_2\text{O})_8]^{3+}$ hydration species as a reactant (shown in Table S2†) and in our recent DFT study related to the selectivity by using chalcogen-donor ligands.¹⁵ We have also demonstrated the calculation of the complexes with the different conformations which were obtained by replacing the starting coordinate of the optimized geometry of X = N with X = P, As, and Sb (Fig. S1–6 and Table S3†). The values of $\Delta G(\text{Am}) - \Delta G(\text{Eu})$ also indicated the same tendency with the variation of X to the results in Table 2.

Population analyses of $[\text{M}(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$

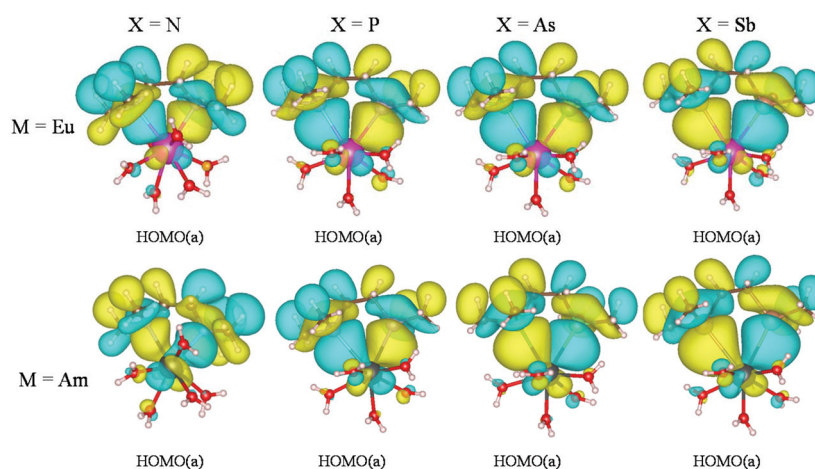
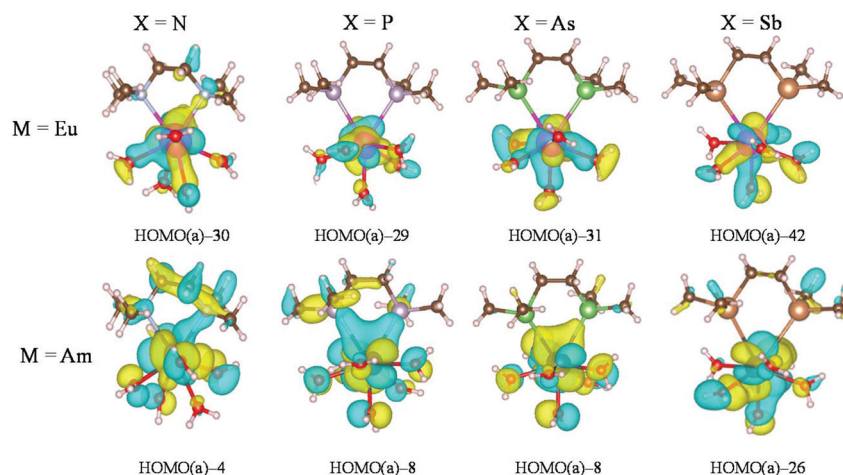
Table 3 shows the Mulliken and natural atomic spin population (ρ_{spin}) values of the metal ions and the donor atoms for the complexes, $[\text{M}(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$. Because the ρ_{spin} values are zero in a non-interaction system between the metal ion and the ligands except for the valence f-orbital electrons in the metal ion, the values enable us to estimate the degree of the electronic interaction between the metal ion and the donor atoms. Focusing on the variation of the ρ_{spin} values of the metal ion from the naked metal ion to the complex, the variation of the Am(III) system is always larger than that of the Eu(III) system in each atomic orbital. This result indicated that the covalent interaction in the metal–ligand bond for the Am(III) complex is stronger than that for the Eu(III) complex. Especially, the contributions of d- and f-orbital electrons were large. Previous studies^{14,15,54} reported that the main contribution to the spin population was the d- or f-orbital electrons for trivalent f-block complexes with phosphinic acid and dithiophosphinic acid ligands which support the present result. Comparing the ρ_{spin} values of the donor atoms, the

Table 3 Atomic spin population, ρ_{spin} , of the metal ions and donor atoms for Mulliken's population method/natural population method

Complexes		ρ_{spin} /electrons					
		s (M)	p (M)	d (M)	f (M)	All (X)	All (O)
X = N	M = Eu	0.007/0.004	0.013/0.001	0.035/0.030	5.995/5.830	-0.030/0.009	-0.018/0.093
	M = Am	0.012/0.005	0.014/0.002	0.052/0.030	5.972/5.863	-0.035/0.025	-0.021/0.073
X = P	M = Eu	0.009/0.005	0.016/0.001	0.045/0.035	5.997/5.946	-0.040/-0.015	-0.021/0.027
	M = Am	0.014/0.008	0.018/0.002	0.064/0.045	5.975/5.924	-0.049/0.040	-0.020/0.047
X = As	M = Eu	0.008/0.005	0.016/0.001	0.044/0.035	5.996/5.950	-0.033/0.026	-0.022/0.028
	M = Am	0.014/0.008	0.017/0.002	0.062/0.044	5.975/5.928	-0.040/0.031	-0.021/0.045
X = Sb	M = Eu	0.008/0.006	0.016/0.001	0.047/0.038	5.997/5.960	-0.033/0.027	-0.022/0.024
	M = Am	0.013/0.008	0.017/0.002	0.064/0.046	5.977/5.940	-0.036/0.029	-0.022/0.039

values of the pnictogen-donor atoms were varied depending on the metal ions and pnictogen atoms for both Mulliken and natural population results. The contribution of the ρ_{spin} of the phosphorus atom to the covalency is the largest, especially for the Am(III) complexes. This tendency was observed to be different in the case of hexavalent uranium complexes, $[\{\text{N}(\text{CH}_2\text{CH}_2\text{NSi}^i\text{Pr}_3)_3\}\text{U}(\text{VI})\text{X}]$ (X = N, P, As, and Sb), whose

bond critical point values decreased in the order of X = N, P, As, and Sb.⁵⁸ This might have originated from the hardness or softness of the actinide ions. The tendency observed in U(VI) complexes corresponds to the hard acid classification; however, that in Am(III) complexes corresponds to the soft acid classification in the HSAB rule.³ This result implies that the slight softness character of Am(III) ions compared to U(VI) ions

**Fig. 3** Selected d-type MO surface descriptions of the complexes, $[\text{M}(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$.**Fig. 4** Selected f-type MO surface descriptions of the complexes, $[\text{M}(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$.

in the complexes causes the tendency towards the soft acid classification for pnictogen-donor ligands due to some covalent contributions of d- or f-orbital electrons.

The surface descriptions of the selected d- and f-orbital type MOs for the complexes, $[M(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$, are shown in Fig. 3 and 4, respectively. In Fig. 3, the d-type MO surfaces have a similar shape of the orbital overlap between the metal ion and the pnictogen atoms among all complexes as the bonding-type, in which the orbital overlap is observed with the same phase, regardless of the difference in the DMXE chelating type between $X = \text{N}$ and the others. On the other hand, the f-type MO shapes in Fig. 4 were observed to be different among the complexes. In the case of the $\text{Eu}(\text{III})$ complexes, there are almost no MO overlaps between the metal-pnictogen, whereas in the case of the $\text{Am}(\text{III})$ complexes, the $\text{Am}(\text{III})$ ions

exhibit the bonding-type MO overlaps with the N- and P-donor atoms and no overlaps with the As- and Sb-donor atoms. Focusing on the metal–oxygen bonds, $\text{Eu}(\text{III})$ ions exhibit bonding-type overlaps, whereas $\text{Am}(\text{III})$ ions exhibit antibonding-type overlaps, in which the orbital overlap is observed with the opposite phase. This difference in bonding properties with O-donor atoms between $\text{Eu}(\text{III})$ and $\text{Am}(\text{III})$ ions has been discussed in our previous studies as an origin of $\text{Eu}(\text{III})$ ion selectivity over $\text{Am}(\text{III})$ ions by O-donor ligands,^{12–15} although the difference has no significant effect on the covalent interaction between the metal ion and the pnictogen-donor atoms.

In order to discuss systematically the bonding overlaps between the metal ion and the pnictogen-donor atoms, we analyzed the density of states (DOS) and MO overlap population (MOOP) for the complexes, $[M(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$, using

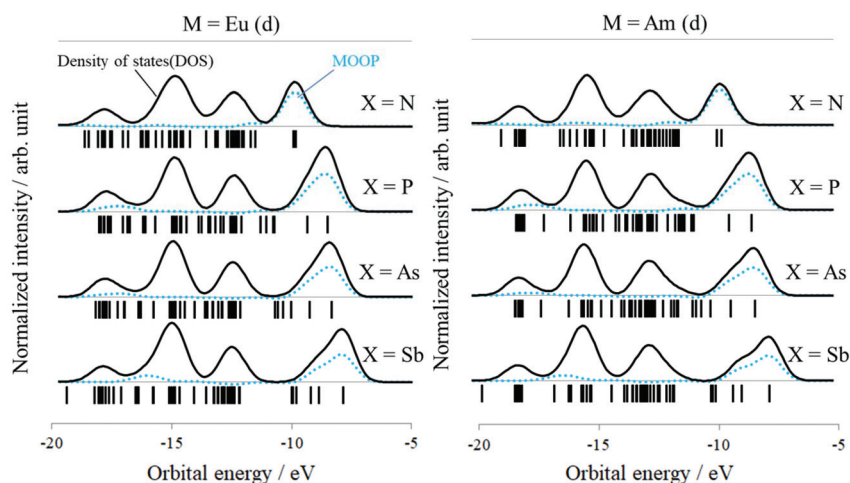


Fig. 5 Density of states (DOS) curves of the metal d-orbital electrons and MO overlap population (MOOP) curves between the metal d-orbital and the donor atoms for the complexes $[M(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$, shown as black solid curves and dotted blue curves, respectively. Black bars below the DOS curves describe the MO energy.

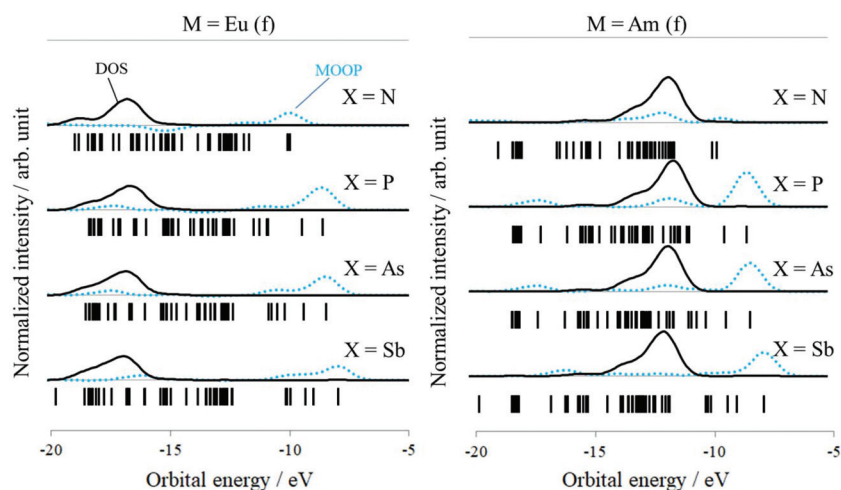


Fig. 6 Density of states (DOS) curves of the metal f-orbital electrons and MO overlap population (MOOP) curves between the metal f-orbital and the donor atoms for the complexes $[M(\text{DMXE})(\text{H}_2\text{O})_6]^{3+}$, shown as black solid curves and dotted blue curves, respectively. Black bars below the DOS curves describe the MO energy.

the same procedure as in our previous studies^{12–15} and the numerical data are shown in Tables S4–11.† Partial DOS curves of the atomic orbitals in the metal ion are shown as black solid lines for d- and f-orbitals in Fig. 5 and 6, respectively. MOOP curves between the atomic orbitals of the metal ion and the pnictogen donor atoms are shown as blue dotted lines for the d- and f-orbitals in Fig. 5 and 6, respectively. These curves were described as the superposition of Gaussian lines convoluted by the half-width of 0.5 eV. The partial DOS curves and MOOP curves of the d-orbitals for Eu(III) and Am(III) complexes showed almost the same distribution irrespective of the difference in the pnictogen-donor atoms (Fig. 5). This result indicated that the d-orbitals of the metal ions participate in the coordination bond with the pnictogen atoms; however it hardly affects the Am(III)/Eu(III) selectivity, which is comparable to the discussion on the MO surface descriptions. This result was consistent with our previous work^{14,15} which indicated that the overlap population curves of the d-orbital have the same character for Eu and Am systems with chalcogen-donor ligands. We focus on the orbital energy region to which the partial DOS curve of the f-orbitals for the metal ion contributes as shown in Fig. 6. It was indicated that Eu(III) and Am(III) ions have almost no interaction with the pnictogen atoms except for the complexes, [Am(DMNE)(H₂O)₆]³⁺ and [Am(DMPE)(H₂O)₆]³⁺, in which the small bonding-type interactions were observed. In the previous work,^{14,15} the overlap population curves of the f-orbital indicated the significantly different character for the Am system that oxygen-donor atoms have anti-bonding-type interactions, but sulfur-donor atoms have bonding-type interactions with the Am 5f-orbital. This difference in the bonding interaction was implied to be an origin of Am(III)/Eu(III) selectivity. The present study also indicates the difference in the Am 5f bonding characters with pnictogen-donor atoms. We suggest that the small contribution to the covalency in the Am(III) complexes is an origin of the Am(III)/Eu(III) selectivity by the DMXE ligands.

Conclusions

We modeled the complexes, [M(DMXE)(H₂O)₆]³⁺ (M = Eu and Am; X = N, P, As, and Sb), to rationalize the Am(III)/Eu(III) selectivity by pnictogen-donor atoms with the metal–pnictogen bonding properties using DFT calculations. The model complexes were obtained with similar geometries to a square antiprism coordination sphere. The hard acid character of Eu(III) and Am(III) ions was indicated by comparing the Δr values and the tendency of the Gibbs energy difference (ΔG) for the complexation reaction, N < P < As < Sb. The Am(III)/Eu(III) selectivity was demonstrated by the difference of ΔG between Eu(III) and Am(III) systems. It was indicated that the N- and P-donor ligands exhibit Am(III) selectivity over Eu(III). The tendency in the Am(III) selectivity was obtained as P > N > As > Sb, which is comparable to the soft acid classification in the HSAB rule. The Am(III) selectivity by N- and P-donor ligands was caused by the slightly stronger covalent interactions between the metal

and the donor atoms for Am(III) complexes than that for Eu(III) complexes deduced by means of Mulliken's population analyses. Furthermore, we concluded that the f-orbital contribution to the covalency in the metal–ligand bonds is an origin of the slightly softer acid character of Am(III) ions and correlated with the Am(III)/Eu(III) selectivity by the pnictogen-donor ligands by means of MO surface and MOOP analyses. This conclusion strengthened our previous discussions about the selectivity and covalent relationship and enabled us to reconfirm the importance of the bonding evaluation in detail between the metal ion and the ligands, leading to the novel ligand design.

Conflicts of interest

There are no conflicts to declare.

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