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PAPER

Computational study of An-X bonding (An = Th, U; X = p-block-based ligands) in pyrrolic macrocycle-supported complexes from the quantum theory of atoms in molecules and bond energy decomposition analysis

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A systematic computational study of organoactinide complexes of the form [LAnX]ⁿ⁺ has been carried out using density functional theory, the quantum theory of atoms in molecules (QTAIM) and Ziegler-Rauk energy decomposition analysis (EDA) methods. The systems studied feature L = *trans*-calix[2]benzene[2]pyrrolide, An = Th(IV), Th(III), U(III) and X = BH₄, BO₂C₂H₄, Me, N(SiH₃)₂, OPh, CH₃, NH₂, OH, F, SiH₃, PH₂, SH, Cl, CH₂Ph, NHPH, OPh, SiH₂Ph, PHPh₂, SPh, CPh₃, NPh₂, OPh, SiPh₃, PPh₂, SPh. The PBE0 hybrid functional proved most suitable for geometry optimisations based on comparisons with available experimental data. An-X bond critical point electron densities, energy densities and An-X delocalisation indices, calculated with the PBE functional at the PBE0 geometries, are correlated with An-X bond energies, enthalpies and with the terms in the EDA. Good correlations are found between energies and QTAIM metrics, particularly for the orbital interaction term, provided the X ligand is part of an isoelectronic series and the number of open shell electrons is low (*i.e.* for the present Th(IV) and Th(III) systems).

Introduction

The organometallic chemistry of the early actinides has been the focus of significant attention for a number of years^{1–10} and, in particular, covalency in the f-block has been the subject of much debate both experimentally and theoretically.^{11–13} Traditional wisdom holds that there may be significant covalency in the bonding in transition metal and early actinide complexes, although the lanthanides and later actinides are generally more ionic in character.¹⁴ However, such descriptions are constantly being reassessed¹⁵ as new systems are synthesised and characterised,^{16–19} and even the nature of covalency (overlap-driven vs energy-driven) has recently come under intense scrutiny.^{11, 20, 21}

Bis-arene complexes of thorium and uranium, recently synthesised and studied by Arnold *et al.*,³ are the focus of this paper. More specifically the bis-arene motif in question is present in the *trans*-calix[2]benzene[2]pyrrolide (L²⁻) ligand, the neutral form of which is shown in figure 1. The pyrrole rings can bond with the actinides in a κ¹: κ¹ fashion via the N, whilst the arene rings bond in an η⁶:η⁶ mode. Such a mode was first found in Sm(III) complexes²² but has

since been seen in U(III), U(IV) and Th(IV) complexes, the latter two also being able to exhibit κ⁵: κ⁵ bonding with the pyrrole rings³ due to the flexibility of this ligand arising from lack of conjugation on the dimethyl linkers.²³

Recent developments by Arnold *et al* have involved the synthesis of complexes with the L²⁻ ligand in an η⁶: κ¹: η⁶: κ¹ bonding mode with B-, N- and O-based ancillary ligands. These include [U^{III}(L)N(TMS)₂] (TMS = tetramethylsilane), [U^{III}(L)BH₄],²⁴ [U^{III}(L)DTBP] (DTBP = 2,6-di-*tert*-butylphenoxide) and [Th^{IV}(L)N(TMS)₂]⁺.²⁵ These complexes take

Fig.1. Neutral form of *trans*-calix[2]benzene[2]pyrrolide with hydrogens on the nitrogens. Image taken from reference 3.

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the general form LANX, and this family provides an excellent opportunity to probe computationally the bonding of the actinides to the X-type ligand where the ligating atom in X becomes progressively more electronegative from boron to oxygen. We here examine this range of An-X bonding, using two computational approaches: the quantum theory of atoms in molecules (QTAIM)²⁶ and energy decomposition analysis (EDA),^{27, 28} each of which is now summarised.

The QTAIM analyses the topology of the electron density (ρ). The lowest point of ρ along a line of locally maximum density between two nuclei (the bond path)²⁹ is known as the bond critical point (BCP). ρ at the BCP below 0.1 e bohr⁻³ is considered indicative of an ionic bond and above 0.2 e bohr⁻³ of a covalent bond.³⁰ The energy density at the BCP (H) is another metric which gives insight into the nature of the bond. When there is significant sharing of electrons, H is negative (reflecting the excess of local potential energy over kinetic energy), and its magnitude reflects the extent of covalency.³¹ Finally for our purposes, the delocalisation index between atoms A and B $\delta(A,B)$ gives the number of electrons shared between two atomic basins and is a measure of the bond order between two atoms.³² The QTAIM has been previously applied to a range of actinide-ligand and other metal-ligand bonds^{18, 33-39} and it has been concluded that while An bonding is predominantly ionic, covalency differences across the 5f series can be distinguished.

Another useful computational technique for analysing metal-ligand bonding is the EDA approach where the complex or molecule in question is fragmented about the bond of interest. In the EDA, the total bond energy (E_B) is broken down as follows:

$$E_B = E_E + E_P + E_O \quad (1)$$

where E_E , E_P and E_O are the electrostatic interaction, Pauli repulsion and orbital mixing terms respectively. The E_E component is obtained from the superimposed unperturbed fragment electron densities and corresponds to the effects of Coulombic attraction and repulsion. This is typically dominated by nucleus-electron attractions, and hence is a stabilising term. E_P is obtained by ensuring that the Pauli principle is satisfied, and this destabilising term is responsible for describing steric repulsion. Finally the stabilising E_O component is obtained from the relaxation of the electronic structure to self-consistency by the mixing of occupied and unoccupied orbitals on each fragment.⁴⁰ What information the EDA provides on covalency is contained within the E_O term.

Links between QTAIM metrics and bond energy data have been found in the past. For example, linear relationships between the hydrogen bond energies and QTAIM data were observed in hydrogen fluoride and nitrile complexes^{41, 42} and, more relevant to this work, relationships have been found for heavy metal and actinide bonding. Studies on dimeric M_2X_6 systems ($M = Mo, W, U$; $X = Cl, F, OH, NH_2, CH_3$) showed correlations between the QTAIM metrics at the bond critical points of the M-M bonds with the M-M

bond energies (obtained with EDA), and also with M-ligand bonds in $(CO)_5M$ - units bonded to three different tautomers of imidazole (where $M = Cr, Mo, W$).⁴⁰ These correlations, however, were found only when the electrostatic and Pauli energies summed approximately to zero, meaning that the vast majority of the total bond energy arose from the orbital mixing term.

This paper reports a systematic computational study of $[LANX]^{n+}$ complexes, where $n = 1$ (Th(IV)) and 0 (Th(III), U(III)), in which L^{2-} adopts the $\eta^6: \kappa^1: \eta^6: \kappa^1$ bonding mode, with focus on the QTAIM analysis of the An-X bond and possible correlations of these QTAIM data with the An-X bond strength and its decomposition. In addition to the intrinsic interest in understanding the relationships between these two rather different approaches to analysing molecular electronic structure and bonding, we note that QTAIM calculations are typically more straightforward to perform than bond energy calculations and decompositions, particularly for systems with several unpaired electrons. Thus, if clear links between QTAIM properties and bond energy terms can be further established, we may arrive at a situation in which we need only calculate QTAIM metrics to gain insight into actinide-ligand bond strengths and covalency.

Computational details and target systems

Geometry optimisations were carried out using Kohn-Sham density functional theory in the Gaussian 09 code (revision D.01)⁴³, using the generalised gradient approximation in the form of the PBE functional⁴⁴ and also the hybrid functional PBE0.⁴⁵ Dunning's correlation consistent polarised valence triple- ζ quality basis sets (cc-pVTZ)⁴⁶ were used for all light atoms (B, C, N, O, F, Si, P, S and Cl), except for hydrogen where the polarised valence double- ζ (cc-pVDZ) quality basis set⁴⁷ was used, and Stuttgart/Bonn quasi-relativistic 60 core-electron pseudopotentials and their associated valence basis sets were used for thorium^{48, 49} and uranium.^{48, 50} The ultra-fine integration grid was used. Frequencies calculations were used to determine if stationary points were true minima, and to obtain thermodynamic corrections to the self-consistent field (SCF) energies.

The Amsterdam Density Functional (ADF) software package⁵¹⁻⁵³ was used for the EDA analysis, and for these calculations the PBE functional was used in single point calculations at the optimised geometries of the PBE0-based full complexes and the LAN^{n+} ($n = 1$ for Th(III) and U(III) and 2 for Th(IV)) and X^- fragments carried out in Gaussian. PBE0 calculations in ADF failed to converge the SCF. For Th(III) and U(III), since both the complexes and their LAN^+ fragments are open-shell, a spin restricted single point calculation on the LAN^+ fragments was first needed, followed by an unrestricted single point calculation at the same fragment geometry with an accompanying EDA calculation. This produced a correction energy term which was subtracted from the E_O and E_B energies obtained in the full EDA calculation of the LANX complex, which was performed spin restricted.⁵⁴

All light atoms in ADF were treated with triple- ζ quality Slater type orbital basis sets with one set of polarisation functions (TZP) and for the actinides with all-electron quadruple- ζ basis sets with four polarisation functions (QZ4P). Scalar-relativistic effects were incorporated by means of the zeroth-order regular approximation (ZORA).⁵⁵⁻⁵⁷

QTAIM calculations were carried out using AIMQB (Version 14.11.23, Professional) and their results analysed in AIMStudio (Version 14.11.23, Professional) from the AIMAll software package.⁵⁸ Integrated properties (for obtaining $\delta(A,B)$) were carried out on the actinide centres and the ligating X-atom only (for the LAnBH_4 complexes, the An, the boron and two bridging hydrogens were integrated). The .wfx input files needed for AIMQB were generated in Gaussian 09 from single point calculations at the optimised geometries.

The $[\text{LAnX}]^{n+}$ complexes were simplified so that the methyl groups in L^{2-} were replaced with hydrogens, and any methyl groups in the X ligands not directly involved in actinide bonding were also replaced with hydrogens, *i.e.* $\text{N}(\text{TMS})_2$ became $\text{N}(\text{SiH}_3)_2$ and DTBP became OPh. We therefore initially had fifteen $[\text{LAnX}]^{n+}$ complexes, where An = Th(IV), Th(III) and U(III) and X = BH_4 , $\text{BO}_2\text{C}_2\text{H}_4$, CH_3 , $\text{N}(\text{SiH}_3)_2$ and OPh, as shown schematically in figure 2; note the η^6 : κ^1 : η^6 : κ^1 conformation of L.

Subsequent calculations were carried out where the X ligand series was modified such that only the ligating atom changed across the p-block in the first and second row, with its chemical environment being hydrogen based, phenyl based, or a mixture of the two, as shown in the list of all the X ligands employed below:

- **X ligands;** BH_4 , $\text{BO}_2\text{C}_2\text{H}_4$, CH_3 , $\text{N}(\text{SiH}_3)_2$ and OPh.
- **X' ligands;** CH_3 , NH_2 , OH and F.
- **X'' ligands;** CH_2Ph , NPh and OPh.
- **X* ligands;** SiH_3 , PH_2 , SH and Cl.
- **X** ligands;** SiH_2Ph , PhPh and SPh.
- **X[†] ligands;** CPh_3 , SiPh_3 , NPh₂, PPh₂, OPh and SPh.

Fig.2. Schematic of $[\text{LAnX}]^{n+}$ complex.

This study therefore reports the analysis of the An-X bonding in a total of fifty six complexes.

Results and discussion

Mean absolute deviation (MAD) analysis of key bond lengths and angles in the $[\text{LAnN}(\text{SiH}_3)_2]^{n+}$ (An = Th, $n = 1$; U, $n = 0$), LUBH_4 and LUOPh complexes, from both PBE and PBE0-based geometry optimisations, with crystallographic data for $[\text{LTh}^{\text{IV}}\text{N}(\text{TMS})_2]^+$, $\text{LU}^{\text{III}}\text{BH}_4$, $\text{LU}^{\text{III}}\text{N}(\text{TMS})_2$ and $\text{LU}^{\text{III}}\text{DTBP}$ (see tables S1 and S2 in the supplementary information) showed that PBE0 gave better results (see tables S3 to S9 for MAD analysis). The Th(III) complexes were also then optimised at the PBE0 level (see table S10 in the S.I.). Note that for the $\text{LTh}^{\text{IV}}\text{BH}_4$ and $\text{LU}^{\text{III}}\text{BH}_4$ complexes, the bonding of the BH_4 group was initially modelled in the An-(μ -H)₃-BH binding mode, but differences in the An-B bond lengths when compared with experiment suggested that we should explore the An-(μ -H)₂-BH₂ binding mode, which was found to agree better with experimental geometry data. This (μ -H)₂ orientation was then analysed with the QTAIM and EDA.

The strength of the An-X interaction

From the PBE0-optimised geometries of the LAn^{n+} and X⁻ fragments, together with the previously optimised full complexes, the An-X ΔE and ΔH_{298} have been calculated for $[\text{LAnX}]^{n+}$ and are given in table 1. These energies are based on the fragment energy data in tables S11 to S14 and are calculated according to the following equations:

$$\Delta E = E^{[\text{LAnX}]^{n+}} - (E^{\text{LAn}^{n+}} + E^{\text{X}^-}) \quad (2)$$

$$\Delta H_{298} = H_{298}^{[\text{LAnX}]^{n+}} - (H_{298}^{\text{LAn}^{n+}} + H_{298}^{\text{X}^-}) \quad (3)$$

where all E terms are the total SCF energies and all H_{298} terms are the SCF energies plus zero-point energy corrections plus thermal corrections to enthalpy (at 298 K).

All of the bonds in table 1 are very strong, the strongest being that between Th and CH_3 in $[\text{LTh}^{\text{IV}}\text{Me}]^+$.

Table 1. An-X energies (eV) for the $[\text{LAnX}]^{n+}$ complexes where $n = 1$ (Th(IV)) and 0 (Th(III) and U(III)), from the LAn^{n+} ($n = 2$ for Th(IV) and 1 for Th(III) and U(III)) and X⁻ fragments.

X	ΔE			ΔH_{298}		
	Th(IV)	Th(III)	U(III)	Th(IV)	Th(III)	U(III)
BH_4	-9.33	-5.44	-5.64	-9.16	-5.34	-5.53
$\text{BO}_2\text{C}_2\text{H}_4$	-10.98	-6.83	-6.85	-10.81	-6.75	-6.75
Me	-11.54	-7.28	-7.37	-10.39	-7.20	-7.26
$\text{N}(\text{SiH}_3)_2$	-9.87	-5.68	-5.66	-9.76	-5.60	-5.55
An-OPh	-10.50	-5.92	-6.16	-10.37	-5.92	-6.06

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This is also the strongest bond for the sets of Th(III) and U(III) complexes. The An-(μ -H)₂BH₂ bond is the weakest. Note that the An-X bond strengths for the Th(III) and U(III) complexes are more similar than those between the Th(III) and Th(IV) complexes, as expected considering the Th(IV) fragment has a 2+ charge to which the X⁻ ligand will bind more strongly compared with the 1+ charge of the Th(III) and U(III) fragments.

Correlation of the An-X bond energies with the QTAIM metrics

As noted in the Introduction, in previous work an approximately linear correlation was found between the metal-ligand binding energy and the QTAIM metrics at the metal-ligand BCP. The present systems however, show only very poor linear correlations between the bond energies in table 1 and the corresponding QTAIM metrics (see table S15 in S.I. for these QTAIM data) as shown in figure 3 for ΔH_{298} . R^2 values for these correlations are 0.031, 0.310 and 0.218 for ρ , H and $\delta(\text{An-X})$ respectively, indicating that the correlations found previously⁴⁰ are by no means general. ΔE gives similarly poor correlations with these QTAIM metrics, with R^2 values of 0.028, 0.301 and 0.211 for ρ , H and $\delta(\text{An-X})$ respectively.

Close inspection of figure 3 shows that for all three sets of actinide complexes, there is an approximately linear relationship between the QTAIM parameters and the bond energies for the boron and carbon-based ligands, but then the trend diverges from this relationship when changing the X ligand to the nitrogen and oxygen based ligands resulting in little overall correlation.

To probe the functional dependence of the above conclusions, single point calculations were carried out on the PBE0-optimised fragments and full complexes using the PBE functional. These ΔE and QTAIM data are presented in tables S16 and S17 and figure S1 in the S.I. As can be seen, although the values are slightly different from the PBE0 data, the overall patterns found in figure 3 are still present in figure S1, and hence we conclude that the QTAIM metrics are essentially uncorrelated with bond energy data for the An-X interactions at either the PBE0 or PBE level.

Comparison of EDA results with QTAIM metrics

The PBE QTAIM metrics (table S17) were next compared with EDA data for the same set of 15 [LAnX]^{nt} complexes. These EDA data, also calculated using the PBE functional at the PBE0 geometries, are presented in tables 2 to 4. E_B follows a similar trend to the ΔE and ΔH_{298} values in table 1; the values increase in absolute terms from the boron to carbon-based ligand but then decrease at nitrogen, yet increase again for the oxygen-based ligand. The break-down of E_B shows, however, that this trend is unique to the total energy since the E_V , E_P and E_O terms all show different trends as a function of X-ligand, and unlike with E_B , the trends in these differ depending on which actinide and oxidation state is present.

Fig.3. An-X bond enthalpies (ΔH_{298}) against An-X BCP electron densities (top), energy densities (middle) and delocalisation indices (bottom). For the different actinides, circles = [LTh^{IV}X]⁺, triangles = LTh^{III}-X and squares = LU^{III}-X. For the different X ligands, blue = BH₄, orange = BO₂C₂H₄, green = Me, purple = N(SiH₃)₂ and red = OPh

For E_V , the largest energy is seen for the Th^{IV}-Me bond (table 2), whereas for the Th(III) and U(III) complexes the An-BO₂C₂H₄ gives the largest E_V value. This is also true for the E_P term, whereas the E_O term is different altogether; there is a steady increase in energy as a function of X ligand for the Th(IV) complexes, but for Th(III) and U(III) there is no apparent trend at all, with the An-BO₂C₂H₄ bond giving the largest E_O value for Th(III), and An-Me giving the largest E_O value for U(III).

These EDA terms are plotted against the PBE-based QTAIM metrics (table S17) in figures S2 to S5. As can be seen from figure S2, the graphs for E_B are very similar to the graphs in figure 3 (and figure S1). Close inspection of figure S3 reveals strong correlation of the [LTh^{IV}X]⁺ complexes' QTAIM metrics with the orbital mixing energy term (the best correlation being with the Th-X electron density with

an R^2 value of 0.938) but this is the exception; in general the QTAIM metrics for the rest of the complexes do not correlate with the EDA data.

We wondered if the general lack of correlation across the EDA energies arises from the X ligand as a whole, rather than the atom ligating directly to the actinide centre. So far the chemical environment of the X ligands have been significantly different, bar the actual ligating atom, *i.e.* the X ligands contain pinacolato, hydrogen, silane and phenyl groups. In the correlations found between EDA data and QTAIM metrics reported previously,⁴⁰ the ligands in question were all of similar chemical nature as they were either tautomers of imidazole bonded to (CO)₅M- units, or followed an isoelectronic series in the case of M₂X₆ where X = CH₃, NH₂, OH, F and Cl. To test this hypothesis, a new set of complexes were modelled with simplified X ligands, labelled X'.

We first focussed on the Th(IV) complexes, so that the new set of complexes were [LThMe]⁺, [LThNH₂]⁺, [LThOH]⁺ and, to extend the series, [LThF]⁺. Boron-based ligands were omitted since, for the BH₄ complex, there is no direct Th-B bond, and there is no other suitable boron-based candidate that would both satisfy the isoelectronicity of this series of X' ligands and have a direct bond with the actinide centre.

Table 2. Th-X EDA energies (eV) for the [LTh^{IV}X]⁺ complexes from the LTh²⁺ and X' fragments.

X	E_B	E_E	E_P	E_O
BH ₄	-9.36	-10.76	4.61	-3.21
BO ₂ C ₂ H ₄	-10.82	-16.13	9.65	-4.34
Me	-11.33	-16.97	10.04	-4.41
N(SiH ₃) ₂	-10.40	-13.04	8.17	-5.53
OPh	-10.69	-12.08	7.49	-6.10

Table 3. Th-X EDA energies (eV) for the LTh^{III}X complexes from the LTh⁺ and X' fragments.

X	E_B	E_E	E_P	E_O
BH ₄	-5.75	-7.48	4.74	-3.01
BO ₂ C ₂ H ₄	-6.95	-15.03	15.18	-7.09
Me	-7.40	-13.04	9.82	-4.18
N(SiH ₃) ₂	-6.41	-9.44	7.55	-4.52
OPh	-6.48	-9.65	9.62	-6.45

Table 4. U-X EDA energies (eV) for the LU^{III}X complexes from the LU⁺ and X' fragments.

X	E_B	E_E	E_P	E_O
BH ₄	-5.80	-3.80	5.65	-7.65
BO ₂ C ₂ H ₄	-6.97	-12.91	9.55	-3.60
Me	-7.42	-1.12	6.71	-13.02
N(SiH ₃) ₂	-6.10	-8.65	6.36	-3.81
OPh	-6.51	-9.46	9.01	-6.06

As above, single point calculations on the PBE0-optimised geometries of [LThX']⁺ were carried out with the PBE functional to obtain EDA and QTAIM data, which are presented in tables 5 and 6. The former shows that E_B and E_O both increase from C to O then decrease at F. This pattern is seen for the $\delta(\text{Th},\text{X})$ values and, to a lesser extent, H in table 6. On the other hand, E_E and E_P both show a clear trend of a decrease, in absolute terms, across this ligand series; a trend mirrored in ρ in table 6.

Analysis of the [LAnX']ⁿ⁺ complexes was extended to the Th(III) and U(III) variants, with the results also given in tables 5 and 6. The R^2 values for correlations between the data in these two tables are collected in table 7. In general, the thorium complexes show the better correlations of EDA energies with the QTAIM metrics compared with the uranium complexes, with the Th(III) complexes showing overall the best R^2 values; the lowest R^2 for ρ vs EDA energy is 0.786 (for E_B), 0.856 for H vs E_E and 0.604 for $\delta(\text{Th}-\text{X})$ vs E_P . For the Th(IV) complexes, the delocalisation indices correlate very well for both E_B and E_O , whereas the electron and energy densities correlate less well. Note that these correlations are found for E_B and E_O despite the E_E and E_P terms not cancelling to near zero, which was a prerequisite for the good correlations of E_B and E_O with QTAIM metrics see in our previous work.⁴⁰ The electron density gives the best correlation with both E_E and E_P , with $\delta(\text{Th},\text{X})$ giving the poorest correlations with R^2 values of 0.562 and 0.749 for E_P and E_E respectively. This is the opposite of what was found with the E_B and E_O data.

For the U(III) complexes, all three QTAIM metrics show appreciable correlations with the E_B and E_O data but E_E has the poorest linear correlation for the U(III) QTAIM metrics, whereas for the U(III) E_P data, there is no discernible trend at all with the QTAIM metrics.

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Table 5. An-X' EDA energies (eV) for the [LAnX']ⁿ⁺ (*n* = 1 (Th(IV)), 0 (Th(III)) and U(III)) complexes from the LAnⁿ⁺ (*n* = 2 (Th(IV)), 1 (Th(III)) and U(III)) and X' fragments.

X'	<i>E_B</i>			<i>E_E</i>			<i>E_P</i>			<i>E_O</i>		
	Th ^{IV} -X'	Th ^{III} -X'	U ^{III} -X'	Th ^{IV} -X'	Th ^{III} -X'	U ^{III} -X'	Th ^{IV} -X'	Th ^{III} -X'	U ^{III} -X'	Th ^{IV} -X'	Th ^{III} -X'	U ^{III} -X'
CH ₃	-11.33	-7.40	-7.42	-16.97	-13.04	-1.12	10.04	9.82	6.71	-4.41	-4.18	-13.02
NH ₂	-12.29	-8.32	-8.30	-16.12	-12.43	-12.27	9.16	9.32	9.93	-5.32	-5.21	-5.96
OH	-12.51	-8.82	-8.52	-15.08	-11.33	-11.41	8.48	7.96	7.59	-5.91	-5.45	-4.71
F	-12.04	-8.23	-8.10	-14.98	-11.24	-9.20	7.83	8.21	6.36	-5.10	-5.20	-5.26

Table 6. PBE An-X' QTAIM metrics from PBE0-optimised geometries for the [LAnX']ⁿ⁺ (*n* = 1 (Th(IV)), 0 (Th(III)) and U(III)) complexes from the LAnⁿ⁺ (*n* = 2 (Th(IV)), 1 (Th(III)) and U(III)) and X' fragments.

X'	ρ (e bohr ⁻³)			<i>H</i> (Hartrees bohr ⁻³)			$\delta(\text{An-X})$		
	Th ^{IV} -X'	Th ^{III} -X'	U ^{III} -X'	Th ^{IV} -X'	Th ^{III} -X'	U ^{III} -X'	Th ^{IV} -X'	Th ^{III} -X'	U ^{III} -X'
CH ₃	0.089	0.081	0.076	-0.032	-0.028	-0.024	0.678	0.605	0.593
NH ₂	0.111	0.101	0.100	-0.045	-0.036	-0.033	0.818	0.793	0.744
OH	0.125	0.117	0.118	-0.050	-0.043	-0.041	0.918	0.882	0.887
F	0.127	0.116	0.109	-0.049	-0.039	-0.029	0.825	0.768	0.755

When compared with the previous EDA results for the [LAnX']ⁿ⁺ complexes (figures S2 to S5), and focusing only on the C-, N- and O-based ligands in both the X and X' series, one sees generally improved correlations for the X' ligands (tables 8 to 10), although we note that there only are three points in each data set. Except for the *R*² values for *E_B* vs ρ and *H* (table 8), both the [LTh^{IV}X']⁺ and [LTh^{IV}X']⁺ EDA data correlate very well with the QTAIM metrics, with the [LTh^{IV}X']⁺ data correlating better overall. The LTh^{III}X' data also correlate much better than the LTh^{III}X (table 9) with the biggest contrasts found with the *E_P* vs QTAIM metrics. On the other hand, in table 10, it is the LU^{III}X data that correlate much better than LU^{III}X'

for *E_P* vs QTAIM metrics, although the rest of the EDA vs QTAIM metrics *R*² values are much better for the LU^{III}X' complexes.

Spurred on by the improved correlations for the simplified ligands, we explored [LAnX*]⁺ complexes, where the X* ligands are the second row p-block-based ligands SiH₃, PH₂, SH and Cl. As with the LAnX and LAnX' complexes, the LAnX* were optimised at the PBE0 level and their QTAIM and EDA data obtained from PBE calculations at the PBE0 geometries. These data are presented in tables S18 and S19 in the S.I.

Table 7. *R*² values for the EDA energies vs QTAIM metrics for [LAnX']ⁿ⁺ (X'=CH₃, NH₂, OH and F, *n* = 1 (Th(IV)), 0 (Th(III)), U(III)) complexes.

	ρ			<i>H</i>			$\delta(\text{An-X})$		
	Th ^{IV} -X'	Th ^{III} -X'	U ^{III} -X'	Th ^{IV} -X'	Th ^{III} -X'	U ^{III} -X'	Th ^{IV} -X'	Th ^{III} -X'	U ^{III} -X'
<i>E_B</i>	0.677	0.786	0.863	0.825	0.927	0.856	0.930	0.999	0.903
<i>E_E</i>	0.971	0.952	0.728	0.900	0.856	0.642	0.749	0.653	0.703
<i>E_P</i>	0.934	0.920	0.012	0.826	0.895	0.143	0.562	0.604	0.043
<i>E_O</i>	0.621	0.859	0.916	0.752	0.900	0.608	0.961	0.945	0.803

Table 8. R^2 values for EDA energies vs QTAIM metrics for C-, N- and O-based ligands in $[LTh^{IV}X]^+$ (non-italics) and $[LTh^{IV}X']^+$ (italics).

	ρ	H	$\delta(Th,X)$
E_B	0.393 0.962	0.486 0.991	0.817 0.940
E_E	0.849 0.961	0.910 0.914	0.997 0.978
E_P	0.897 0.995	0.947 0.972	0.943 1.000
E_O	0.940 1.000	0.977 0.987	0.959 0.999

Table 9. R^2 values for EDA energies vs QTAIM metrics for C-, N- and O-based ligands in $LTh^{III}X$ (non-italics) and $LTh^{III}X'$ (italics).

	ρ	H	$\delta(Th,X)$
E_B	0.612 0.989	0.770 0.976	0.861 0.999
E_E	0.621 0.949	0.778 0.969	0.867 0.872
E_P	0.000 0.898	0.027 0.927	0.077 0.800
E_O	0.916 0.925	0.797 0.896	0.696 0.981

Table 10. R^2 values for EDA energies vs QTAIM metrics for C-, N- and O-based ligands in $LU^{III}X$ (non-italics) and $LU^{III}X'$ (italics).

	ρ	H	$\delta(U,X)$
E_B	0.232 0.936	0.024 0.918	0.201 0.904
E_E	0.615 0.755	0.058 0.726	0.585 0.703
E_P	0.841 0.113	0.939 0.093	0.863 0.079
E_O	0.297 0.908	0.006 0.888	0.269 0.871

As can be seen from table S18, all E_E and E_P energies decrease as a function of X^* ligand for the Th(IV) complexes, whereas for E_B the energies generally increase from Th-SiH₃ to Th-Cl, and the E_O energies follow no clear trend. The ρ and H metrics (table S19) increase as a function of X^* ligand whereas the $\delta(Th,X)$ metric, as with the E_O energies, follows no clear trend. Table 11 summarises

the correlations found for the X^* series. These are poor for LUX*, but rather better for the Th(IV) and Th(III) complexes, with the exception of E_O vs all three QTAIM metrics for $LTh^{III}X^*$. The EDA vs QTAIM correlations for the Th(IV) complexes show strong linear correlations for the E_B vs all three QTAIM metrics, with all R^2 values above 0.900. The E_O data do not correlate so well with the QTAIM metrics generally, although R^2 for E_O vs $\delta(Th,X)$ is high. E_E and E_P also give good linear correlations with the QTAIM metrics for the Th(IV) and Th(III) complexes. The worst correlations are those found with the delocalisation indices, with R^2 values of 0.782 and 0.799 for E_E and E_P respectively, but these are still better than the $[LTh^{IV}X']^+$ analogues where R^2 values for E_E and E_P vs $\delta(An,X)$ are 0.749 and 0.562 respectively (see table 7).

When correlating all the EDA and QTAIM data for the $[LAnX']^{n+}$ and $[LAnX^*]^+$ together there are no strong trends found, as shown in table 12. Closer analysis reveals that the U(III) data in general correlate the least well, and so the data were re-analysed for just the thorium complexes. The results for E_O are presented in figure 4; the rest of the EDA vs QTAIM data – with the exception of E_B vs ρ – give poor correlations, as presented in table 13.

As with the full data set (table 12), the worst correlation in figure 4 is found with the delocalisation indices, although it is much improved over the full data set with an R^2 value of 0.671. The electron and energy densities now correlate extremely well with E_O , suggesting that, for the Th(III) and Th(IV) X' and X^* complexes, the covalency of the Th–X bond is described consistently by both the EDA and QTAIM approaches.

Summarising, it would appear that by employing consistently simple and isoelectronic X ligands, and focussing only on the change of the ligating atom to the actinide centre, then correlations can be found between EDA and QTAIM data that were absent in the primary set of BH₄, BO₂C₂H₄, CH₃, N(SiH₃)₂ and OPh ligands. The fact that E_O appears to correlate best with the QTAIM metrics, particularly for the Th(III) and Th(IV) systems as shown in figure 4, makes sense, in that the chosen QTAIM metrics are indicators of covalency.

Table 11. R^2 values for the An- X^* EDA energies vs QTAIM metrics for $[LAnX^*]^{n+}$ ($n = 1$ (Th(IV)), 0 (Th(III), U(III)) complexes.

	ρ	H	$\delta(An-X)$
	$Th^{IV}-X^* U^{III}-X^* Th^{III}-X^*$	$Th^{IV}-X^* U^{III}-X^* Th^{III}-X^*$	$Th^{IV}-X^* U^{III}-X^* Th^{III}-X^*$
E_B	0.929 0.345 0.930	0.938 0.476 0.995	0.985 0.229 0.871
E_E	0.981 0.255 0.997	0.973 0.376 0.949	0.799 0.167 0.867
E_P	0.980 0.309 0.938	0.975 0.436 0.968	0.782 0.208 0.800
E_O	0.608 0.419 0.224	0.613 0.551 0.099	0.888 0.296 0.268

Table 12. R^2 values for EDA energies vs QTAIM metrics for all $[\text{LAnX}']^{n+}$ and $[\text{LAnX}^*]^{n+}$ complexes. An = Th(IV), Th(III), U(III); n = 1 (Th(IV)), 0 (Th(III)) and U(III)).

	ρ	H	$\delta(\text{An,X})$
E_B	0.048	0.160	0.097
E_E	0.117	0.115	0.094
E_P	0.271	0.350	0.225
E_O	0.047	0.026	0.006

Table 13. R^2 values for EDA E_B , E_E and E_P terms vs QTAIM metrics for all $[\text{LThX}']^{n+}$ and $[\text{LThX}^*]^{n+}$ complexes (n = 1 (Th(IV)), 0 (Th(III))).

	ρ	H	$\delta(\text{An,X})$
E_B	0.812	0.469	0.390
E_E	0.316	0.426	0.142
E_P	0.325	0.411	0.029

Fig. 4. Th-X ρ (top), H (middle) and $\delta(\text{Th,X})$ (bottom) against E_O for $[\text{LThX}']^{n+}$ complexes. Diamonds = Th(IV) complexes, circles = Th(III) complexes. Solid points are X' ligands: green = CH_3 , purple = NH_2 , red = OH , black = F . Hollow points are X^* ligands: pink = SiH_3 , yellow = PH_2 , brown = SH , blue = Cl .

To test these improved correlations further another set of $[\text{LAnX}']^{n+}$ complexes with an isoelectronic series of phenyl-based X'' ligands was modelled. Phenyl groups were chosen since one of the

experimentally characterised complexes has an arene ring on the X ligand ($\text{LU}^{\text{III}}\text{DTBP}$). As with the other $[\text{LAnX}']^{n+}$ and $[\text{LThX}^*]^{n+}$ complexes, the $[\text{LAnX}']^{n+}$ complexes were optimised with PBE0 and these optimised geometries treated with PBE for the single point QTAIM and EDA calculations. The new set of X'' ligands was thus; CH_2Ph , NPh and OPh and the EDA energies and QTAIM metrics are presented in tables S20 and S21 in the S.I.

The E_B and E_O energy terms steadily increase in magnitude as a function of X'' ligand and this increase is mirrored in the QTAIM metrics in table S21. Although, as with the $[\text{LAnX}']^{n+}$ complexes, E_O gives the best R^2 values against the QTAIM metrics, the trend is weak, with the highest R^2 being for E_O vs ρ at 0.548. As previously, the U(III) data were excluded and the data reanalysed; the results for both analyses are presented in table 14. The previous conclusions found for the X' and X^* ligand sets don't hold as well for the X'' ligand set, in that R^2 shows only modest improvements on the exclusion of the U(III) data, and actually decreases in several cases.

These phenyl-based ligands were then extended to the 2nd row p-block, giving the X'' ligands SiH_2Ph , PHPh and SPh . These EDA and QTAIM results are presented in tables S22 and S23 in the S.I. As with the LAnX'' complexes, the LAnX'' complexes were analysed for correlations of EDA energies vs QTAIM metrics for the full data set of the Th(IV), Th(III) and U(III) systems, and also for just the LThX'' complexes, and these R^2 values are presented in table 15. Unlike the LAnX'' complexes, the LAnX'' show some strong correlations, notably for E_P vs QTAIM metrics for the thorium-only data set and the E_O vs QTAIM metrics for both the thorium-only data set and the full data set.

Finally, a set of phenyl-based ligands were analysed where the X atom's substituents were all replaced with Ph groups. Thus the new set of X ligands – which we call X^+ – are CPh_3 , NPh_2 , OPh , SiPh_3 , PPh_2 and SiPh_3 . Due to the poor correlations of the EDA energies against the QTAIM metrics with the U(III) complexes, as observed previously with the $X - X''$ data sets, only the Th(IV) and Th(III) complexes of LAnX^+ are considered here, and the results for the EDA and QTAIM metrics are presented in tables S24 and S25 in the S.I. The R^2 values for correlations between these data are presented in table 16.

Table 14. R^2 values for EDA energies vs QTAIM metrics for all LAnX^{n+} complexes: non-italics = Th(IV), Th(III) and U(III); italics = Th(IV) and Th(III)

	ρ	H	$\delta(\text{An-X})$
E_B	0.065 0.127	0.205 0.261	0.052 0.140
E_E	0.147 0.194	0.331 0.392	0.123 0.179
E_P	0.326 0.275	0.178 0.095	0.232 0.158
E_O	0.548 0.551	0.411 0.317	0.491 0.486

Table 15. R^2 values for EDA energies vs QTAIM metrics for all LAnX^{n+} complexes: non-italics = Th(IV), Th(III) and U(III); italics = Th(IV) and Th(III)

	ρ	H	$\delta(\text{An-X})$
E_B	0.095 0.336	0.148 0.741	0.002 0.275
E_E	0.253 0.102	0.234 0.470	0.103 0.064
E_P	0.711 0.992	0.758 0.804	0.279 0.989
E_O	0.746 0.745	0.666 0.929	0.634 0.701

Table 16. R^2 values for EDA energies vs QTAIM metrics for all LThX^+ complexes.

	ρ	H	$\delta(\text{An-X})$
E_B	0.180	0.259	0.287
E_E	0.500	0.590	0.525
E_P	0.766	0.658	0.269
E_O	0.682	0.638	0.276

The correlations in table 16 range from poor to good, E_P vs ρ having the largest R^2 value of 0.766. This is a similar observation to that found in table 15, where systems with low ρ value correlate with the Pauli repulsion term of the EDA analysis; for the QTAIM data corresponding to the R^2 values in table 16, all ρ values for Th-X^+ , with the exception of $\text{Th}^{\text{IV}}\text{-NPh}_2$ and $\text{Th}^{\text{IV}}\text{-OPh}$, are below 0.1 e bohr⁻³.

Finally, all the Th(IV) and Th(III) data bar those for the parent X ligands were collated. The strongest correlations were found between the QTAIM data and the E_O energies, and these are shown in figure 5. $\delta(\text{Th-X})$ has a low R^2 value of only 0.408, but the BCP metrics show appreciable R^2 values; it is promising that such a large data set (twenty four compounds) shows good correlations between the QTAIM BCP covalency metrics and the E_O term of the EDA. As with the X' and X^* ligands in figure 4, the correlation of δ with E_O is poorer than for ρ and H .

Fig.5. Th-X ρ (top), H (middle) and $\delta(\text{Th-X})$ (bottom) against E_O for all $[\text{LThX}]^{n+}$ complexes where $\text{X} = \text{X}', \text{X}'', \text{X}^*, \text{X}^{**}$ and X^+ and $n = 1$ (for Th(IV) complexes) and 0 (for Th(III) complexes). Data point for $\text{Th}^{\text{IV}}\text{-CPh}_3$ omitted as it was a significant outlier.

Conclusions

The geometries of all complexes of the type $[\text{LTh}^{\text{IV}}\text{X}]^+$, $\text{LTh}^{\text{III}}\text{X}$ and $\text{Lu}^{\text{III}}\text{X}$, where X includes the X' , X'' , X^* , X^{**} and X^+ ligands, have been optimised at the PBE0 level. The An-X bonds are strong, with the Th(IV) complexes being the most stable due to the cationic LAn^{n+} fragments having a 2+ charge rather than 1+, as is the case for the An(III) systems. Correlation of the bond energies in $[\text{LAnX}]^{n+}$ with the An-X bond critical point ρ and H , and with the An-X delocalisation indices, all calculated at the PBE level, gave low R^2 values. EDA E_B data also showed a lack of clear trend with the QTAIM covalency metrics.

Keeping the chemical environment of the X-ligand consistently isoelectronic (in this case with X' , X'' , X^* , X^{**} and X^+ ligand sets), so

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that the only variable in each set of $[\text{LANX}]^{n+}$ complexes was the ligating X atom, lead to some strong correlations between EDA data and QTAIM metrics, particularly when the U(III) data were excluded. The QTAIM covalency metrics correlated very well with the orbital interaction energies, with the Pauli and electrostatic terms correlating better in systems where the QTAIM metrics showed the lowest level of covalency.

The lack of correlations with the U(III) complexes is probably due to these having a high spin multiplicity, which adversely affects the terms in the EDA. Open shell-closed shell intermolecular interactions are less well understood compared with those between two closed shell fragments⁵⁹. Different approaches to the EDA scheme have been studied for open-shell systems, such as the absolutely localised molecular orbital-EDA⁶⁰ scheme, used to study alkyl radicals and benzene radical cation complexes⁵⁹. More relevant for this present work, the constrained space orbital variation (CSOV) method⁶¹ for both open and closed shell f-block mono aqua complexes, has proved useful for obtaining bond energies for open shell systems, where a polarisation contribution E_{pol} was included in the CSOV EDA method, 10% of which was made up from the polarisation energy of the unpaired electrons⁶². These contributions are clearly not negligible, and it may be that for the ADF-implemented EDA approach, the f-elements with more than one unpaired electron become more difficult to describe compared to their lower spin-state, closed shell counterparts.

In conclusion, the QTAIM metrics are good indicators of covalency between heavy element centres and ligating groups, provided that the ligand is part of an isoelectronic series, and the number of open shell 5f electrons is low.

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Good correlations are found between QTAIM BCP and EDA data for a range of Th(IV)- and Th(III)-p element bonds