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# Dalton Transactions

## PAPER

# On the selectivity of diglycolamide (TODGA) and bis-triazine-bipyridine (BTBP) ligands in actinide / lanthanide complexation and solvent extraction separation – a theoretical approach †,#

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Theoretical calculations (density functional theory with the scalar relativistic ZORA Hamiltonian) have been performed to obtain the energy and Gibbs free energy of formation of cationic 1:3 complexes of americium(III) and europium(III) with a tri-O-dentate diglycolamide ligand TEDGA (model of TODGA extractant), as well as the free energy of their partition between water and an organic diluent. The distribution of electron density over the atoms, bonds, and molecular orbitals was analyzed by means of Mulliken population analysis, localization procedure of natural bond orbitals, and the Quantum Theory of Atoms-in-Molecules. The stabilities of both $[M(TEDGA)_3]^{3+}$ complexes are similar to each other. On the other hand, our recent data for a similar pair of cationic Am/Eu complexes with a softer (HSAB) tetra-N-dentate ligand C2-BTBP show that the $[Am(C2-BTBP)_2]^{3+}$ complex is significantly more stable in aqueous solution than its Eu counterpart. The decisive factor stabilizing the $Am^{3+}$ complexes over their $Eu^{3+}$ analogues is the charge transfer from the ligands, somewhat greater on the $6d(Am^{III})$ than on $5d(Eu^{III})$ orbitals. The covalency of M–N bonds in the $[M(C2-BTBP)_2]^{3+}$ complexes is greater than that of M–O bonds in $[M(TEDGA)_3]^{3+}$, but the latter is not negligible, in particular in the bonds with the oxygen atoms of the amide groups in TEDGA. The analysis of charge distribution over the whole molecules of the complexes shows that the TEDGA molecule is not hard as expected, but relatively soft Lewis base, only slightly harder than BTBP. This conclusion has been confirmed by the calculation of chemical hardness of the ligands. Moreover, the comparison of the results of bonding analysis with the calculated energies of complex formation in water and in the gas phase allows us to conclude that the population analysis, QTAIM topological parameters, and SOPT stabilization energy, as well as Wiberg and overlap-weighted NAO indices are the tools for analyzing covalency rather than the total bond strength.

## Introduction

Selective separation of actinide elements from highly radioactive nuclear waste is a key issue in modern technologies of waste reprocessing.[1] Much attention was paid, therefore, to the complex formation of actinides and lanthanides with ligands of different hardness. Moderately soft (Pearson's HSAB approach) heterocyclic

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orbitals of greatest stabilization energies, $\Delta E(2)$, in the $[M(TEDGA)_3]^{3+}$ complexes. See DOI: 10.1039/b000000x/

poly-N-dentate bis(1,2,4-triazine) ligands: BTP, BTBP and BTPhen; appear to be selective extractants of actinides(III) over lanthanides.[2-5] Quantum mechanical (QM) calculations on the BTP and BTBP complexes indicate predominantly ionic character of the An–N and Ln–N bonds, with somewhat higher covalent contribution into the former, albeit the question of participation of given metal orbitals in the bonding remains controversial, and the origin of the actinide selectivity of aromatic poly-N-donor ligands has not been clearly explained yet.[2-7] Our recent theoretical studies on BTBP complexes of $Am^{III}$ and $Eu^{III}$ ions, in particular bonding analysis with the use of NBO, QTAIM and CMO methodologies, confirm the higher covalency of the Am–N bonds[8] and show that the selectivity of BTBP ligands is probably connected with different overlaps of lone pair orbitals on the donor nitrogen atoms of the ligands with acceptor orbitals on the metal ions, greater for $6d(Am^{III})$ than for $5d(Eu^{III})$, because of a greater spatial range of the former.[9] On the contrary,

harder poly-O-dentate ligands are either not selective or show some preference to lanthanides.[3,4]

The aim of the present work was to rationalize, on the basis of quantum chemical calculations, the lack of actinide selectivity of the tri-O-dentate diglycolamide ligands in solvent extraction separations of $An^{III}$ from $Ln^{III}$ ions. The study was carried out on *N,N,N',N'*-tetraoctyl-diglycolamide (TODGA), the well known extractant of f-electron metals from $HNO_3$ solutions, of some preference to lanthanides over actinides.[10] QM calculations of the formation energies and Gibbs free energies of its extractable Am/Eu complexes were performed together with theoretical analysis of metal-to-ligand bonds in the $Am^{III}$ and $Eu^{III}$ complexes, including electron density distribution and molecular orbitals analysis. The results have been compared with those recently obtained for the $Am^{III}$ and $Eu^{III}$ complexes with moderately soft C2-BTBP ligand.[8,9] Because the better extraction of $Am^{III}$ than $Eu^{III}$ from the aqueous to the organic BTBP phase had been related to the greater stability of the extracted Am-BTBP than Eu-BTBP complexes,[8] we expected somewhat greater stability of the better extracted Eu-TODGA than the Am-TODGA complex. Moreover, the stronger interactions of the harder $Eu^{III}$ cation with harder TODGA ligand would correspond to the HSAB principle. In order to save the computational resources the calculations were carried out on a model ligand, *N,N,N',N'*-tetraethyl-diglycolamide (TEDGA). Another recent theoretical study on two series of $Am^{III}$ and $Eu^{III}$ complexes with homologous BTBP ligands, has shown that the chain length of hydrocarbon substituents in the ligands has a very little impact on the charge distribution and occupancy of metal orbitals in the complexes.[11]

## Computational details

Geometric parameters of the 1:3 $Am^{III}$ and $Eu^{III}$ TEDGA complexes, of the $M^{III}$ nona-aqua cations (for thermodynamic calculations), and of free TEDGA ligand (for calculating partial charges and ionization energies) were optimized at the DFT level of theory with hybrid B3LYP functional[12] by using the Gaussian 09 suite of programs.[13] The data for C2-BTBP were taken from the previous work.[9] To take into account relativistic effects for the heavy metal complexes under study, the inner 60 core electrons of the Am atom were replaced by Stuttgart-Dresden MWB60[14] Effective Core Potential (ECP) and 28 inner core electrons of the Eu atom – by MWB28[15] ECP. For both atoms, the 35 electrons spanning the outer core (5*d*, 6*s*, 6*p* for Am, and 4*d*, 5*s*, 5*p* for Eu) and valence (5*f*, 6*d*, 7*s* and 7*p* for Am, and 4*f*, 5*d*, 6*s* and 6*p* for Eu) space, were treated explicitly with the complementary energy-consistent pseudorelativistic basis set (for Eu – implemented in Gaussian 09 program, and for Am – ANO type valence basis set). For other atoms, the standard Pople-style polarized valence triple-zeta 6-311G** basis set[16] was used for optimization

After geometry optimization, single point energy computations were performed at the DFT (density functional theory) level, with the hybrid B3LYP and GGA PBE[17] functionals and triple zeta Slater type (TZP) basis set, using the ADF2013 package.[18] Gibbs free energies have been calculated with GGA PBE functional and the same basis set. Spin-unrestricted approach with the highest multiplicity (seven) of the $f^6$ metal ions in the complexes was used. To take into account relativistic effects, one-component Zeroth

Order Regular Approximation (ZORA) Hamiltonian[19] was applied. Spin-orbit coupling was neglected during computation not only because of the computational costs, but also because the orbital population analysis had not been implemented for two-component wave functions. For the calculations of single-point energy and Gibbs free energies, solvent (water, trichloroethane) effects were modeled *via* conductor-like screening model (COSMO).[20] To improve SCF convergence, true density in the exchange-correlation potential was used instead of density fitting technique. The "excellent" quality of Becke grid for numerical integration was used during all computations.

The ionization energies of the heavy metal ions were calculated both without (one-component ZORA) and with (two-component ZORA) inclusion of spin-orbit coupling.

Three different approaches were used for bonding analysis:
(1) Mulliken population analysis,[21] using localization procedure of atomic orbitals (AOs) in molecular orbitals (MOs), was applied to calculate partial charges on the atoms in the complexes.
(2) NPA/NBO localization procedure was used to evaluate the partial charges, electronic configurations, donor-acceptor interactions (the Second Order Stabilization Energy) and bond orders (the Wiberg bond index and overlap weighted NAO) in the complexes studied. The NPA/NBO approach employs Natural Orbitals (orbitals with maximum occupancy). All parts of the NBO analysis were carried out by using the NBO 5.0 program.[22]
(3) In the QTAIM (Bader) analysis,[23] partial charges were computed as integrals of electron density over the atomic basins (determined with zero-flux points). Several QTAIM parameters were analyzed in this work: (i) electron density at Bond Critical Point (BCP), $\rho_b$; (ii) its Laplacian, $\triangledown^2\rho_b$; (iii) bonding radius, *i.e.* the distance from the atom to BCP, $R_b$; (iv) bond ellipticity, $\varepsilon_b$; and (v) ion/cov ratio.[24]

## Results and discussion

### Optimized geometry of the complexes

The problem we met at the beginning was to fix the composition (stoichiometry) of the dominant $Am^{III}$ and $Eu^{III}$ TODGA complexes extracted to the organic phase, with the coordination numbers of the central metal ions, CN=9. Unfortunately, experimental speciation data are not available yet. Slope analysis of the data of solvent extraction of trivalent *f*-metal ions from acidic ($HNO_3$) aqueous phase to non-polar organic diluents points to the extraction of 1:3 and 1:4 metal-TODGA species, though different, sometimes sophisticated extraction models were proposed to justify formation of these species.[10,25-27] The main question is whether nitrate anions enter the inner coordination sphere of central metal ions in the complexes or not. Arisaka and Kimura found (TRFS) that the inner coordination sphere of $Eu^{III}$ in the extracted TODGA complex is free of water molecules, and suggested that it was occupied by TODGA and/or $NO_3^-$.[27] Recently, Shi *et al.* reported their QM calculations on the geometrical and electronic structures and on the thermodynamics of 1:1 (neutral) and 1:2 (cationic and neutral) TODGA complexes of $Am^{III}$ and $Eu^{III}$.[28] Given the high stability constants of consecutive Eu-TODGA complexes, determined in the water-ethanol solvent,[29] we assumed that homoleptic 1:3 complexes of $Am^{III}$ / $Eu^{III}$ with TODGA predominated in the system at low $HNO_3$ concentrations,

and therefore our calculations were limited to cationic complexes $[M(TEDGA)_3]^{3+}$ (M = Am$^{III}$ and Eu$^{III}$).
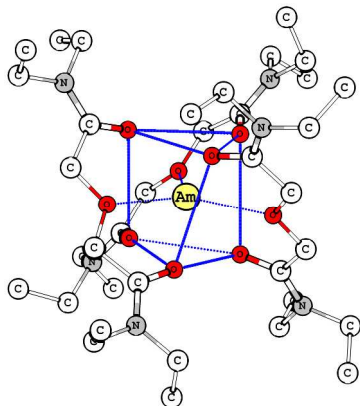


**Fig. 1** The optimized structure of $[Am(TEDGA)_3]^{3+}$. Hydrogen atoms removed for clarity.

**Table 1** Mean metal–ligand distances, d, and selected angles in the $[M(TEDGA)_3]^{3+}$ complexes. The structures were optimized in the gas phase at the B3LYP/MWB/6-311G** level of theory. $O_{eth}$ and $O_{am}$ denote the ethereal and amide oxygen atoms, respectively, in the TEDGA molecule (see Fig. 2).

| M–L | d (Å) | angle | deg |
|------|-------|-------|------|
| Am–$O_{am}$ | 2.46 | $O_{am}$-Am-$O_{eth}$ | 59.8 |
| Am–$O_{eth}$ | 2.65 | $O_{am}$-Am-$O_{am}$' | 119.8 |
| Eu–$O_{am}$ | 2.42 | $O_{am}$-Eu-$O_{eth}$ | 60.6 |
| Eu–$O_{eth}$ | 2.62 | $O_{am}$-Eu-$O_{am}$' | 120.7 |
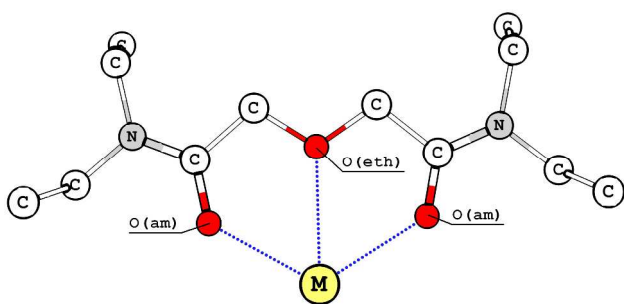


Fig. 2 Schematic coordination of TEDGA (*via* three oxygen atoms) to a metal cation M$^{n+}$. Hydrogen atoms removed for clarity.

Cartesian coordinates of all the atoms in the complex molecules studied are given in Tables S1 and S2†, and the distances between the donor oxygen atoms in the first coordination sphere of the complexes – in Table S3†. Fig. 1 shows the structure of the $[Am(TEDGA)_3]^{3+}$ complex, optimized in the gas phase. The coordination number of the metal ion, CN = 9, is satisfied by the coordination by three tridentate TEDGA ligands. Nine donor oxygen atoms in the first coordination sphere of the metal ion form the

structure of a twisted tricapped trigonal prism. The side faces of the prism resemble slightly deformed rhombs (or rather parallelograms) with short diagonal (the distance between two side oxygen atoms in the ligand) of ~4.2 Å; long diagonal of ~4.8 Å, and edges of ~3.2 Å (sides of both triangles) and ~3.35 Å. A very similar structure, with somewhat shorter M–O and O–O (Table S3†) distances, has been obtained for the analogous $[Eu(TEDGA)_3]^{3+}$ complex.

Though some differences appear between the structures of other Ln/An complexes, optimized in the gas-phase and in the implicit solvent medium,[30-32] our gas-phase structures were not further optimized using solvent medium model, in line with the recommendation by Vallet *et al.*[33] Optimization of large and flexible structures in the polarizable continuum model of solvent is troublesome and often fails, whereas single point energy calculations using this model, combined with the structures optimized in the gas phase usually yield sufficiently good results.

Table 1 presents the calculated metal-ligand bond distances and selected bond angles in the studied complexes. Due to the symmetry of the ligand and complex molecules, only two types of the M–L bonds were analysed: M–$O_{eth}$ (ethereal oxygen) and M–$O_{am}$ (amide oxygens, Fig. 2). The calculated Am–$O_{am}$ and Eu–$O_{am}$ distances in the TEDGA complexes are in good agreement with the reported EXAFS values for the prismatically arranged oxygen atoms in the corresponding nonahydrate cations, but the M–$O_{eth}$ distances are much greater than those for the capping oxygen atoms in the nonahydrates.[34,35] There is no published crystalline structure of $[Eu(TEDGA)_3](NO_3)_3$, but the parameters of our optimized structures of both Am and Eu TEDGA complexes well correspond (except the differences in the ionic radii) to those of the crystalline structure of the La$^{3+}$ complex with a homologous ligand, *N,N,N',N'*-tetra(i-butyl)-diglycolamide.[36] The different La–$O_{am}$ and La–$O_{eth}$ distances in $[La(TiBDGA)_3]^{3+}$ were discussed as typical for other amide and ether complexes,[36] but the difference of the experimental values (*ca*. 0.08 Å) is smaller than that calculated for the 1:3 Eu/Am TEDGA complexes (0.2 Å; Table 1). Similar differences between the M–$O_{am}$ and M–$O_{eth}$ distances, of *ca*. 0.2 Å, have also been computed for the 1:2 TODGA complexes of Am$^{III}$ and Eu$^{III}$.[28]

The gas-phase structures of the free TEDGA molecule (Table S4†; necessary for charge distribution analysis), and of the nona-aqua ions $[Eu(OH_2)_9]^{3+}$ and $[Am(OH_2)_9]$ (Tables S5 and S6†; necessary for calculating the formation energies of the complexes in water), have been optimized at the same level of the theory as the TEDGA complexes (B3LYP/MWB/6-311G**).

**Energy calculations**

Two different models of solvent extraction of metal ions – as neutral and cationic complexes – were discussed in the previous paper.[8] In this case we consider only cationic $[M(TEDGA)_3]^{3+}$ complexes which are formed in the aqueous phase and then they are transferred to the organic phase – in order to satisfy the principle of electroneutrality of each phase – together with the equivalent number of counterions ($NO_3^-$). This model, though probably different from the real process, is correct from the thermodynamic point of view because both the energy and Gibbs free energy are the functions of state so their total changes in the process do not depend on the reaction path. However, in order to have the calculated $\Delta E$

and $\Delta G$ values comparable with the experimental ones, and to be able to use them for interpretation of the experiment by means of QM calculations, formation energies ($\Delta E_{cf}$ and $\Delta G_{cf}$) of the optimized $[M(TEDGA)_3]^{3+}$ complexes were calculated in the system modelling an aqueous solution. Moreover, because the continuum solvent models (e.g. COSMO) alone insufficiently well reflect high energies of solvating the metal ions in their first coordination sphere, the bare $M^{3+}$ ions (the substrates in reactions of complex formation in the gas phase) were additionally explicitly hydrated in the first sphere, with nine water molecules each, giving nonahydrates $[Eu(OH_2)_9]^{3+}$ and $[Am(OH_2)_9]^{3+}$.

On the other hand, to calculate the total energy of ion pair partition one must calculate not only the energy of transfer of counterions ($NO_3^-$) but also the energy of outer-sphere association of the cations with the anions in the organic phase. However, because the equilibrium of the latter process depends on the properties of the ions and the diluent, concentrations etc., the calculation is impossible without using a number of experimental parameters. Because of that, we didn't calculate the total free energies of ion pair partition for the cationic complexes but the difference between the two values for the Am and Eu complexes, $\Delta(\Delta G_{part})_{Am/Eu}$. With this approach, not only the contributions from the transfer of $NO_3^-$ counterions cancel each other, but so do the energies of association of cationic complexes of Am/Eu with nitrate anions (assuming the same degree of association of both ion pairs). Also the impact of much lower hydrophobicity of the TEDGA than TODGA complexes on the thermodynamics of their partition[37] would be canceled in the $\Delta(\Delta G_{part})_{Am/Eu}$ value. By analogy, we also calculated the differences between the other thermodynamic quantities of the $[M(TEDGA)_3]^{3+}$ Am/Eu complexes (Table 2).

The differences in the formation energies of the complexes in water ($\varepsilon = 78.4$), and also in the gas phase, $\Delta(\Delta E_{cf,m})_{Am/Eu}$, were calculated from eq. 1, taking $[M(OH_2)_9]^{3+}$ (m=aq) or $M^{3+}$ (m=g), respectively, as the substrates. Both B3LYP and PBE functionals were used to calculate the formation energies of the species from spherical spin-restricted atoms, $E_i$, while to calculate the respective free energies, $G_i$, the PBE functional was used (Table S7). Table 2 presents also the $\Delta(\Delta G_{cf,aq})_{Am/Eu}$ value as well as the differences between free energies of transfer (partition) of the complexes from water to 1,1,2-trichloroethane (TCE; $\varepsilon = 7.2$), $\Delta(\Delta G_{part})_{Am/Eu}$, (eq. 2), and between free energies of extraction of the Am and Eu ions in the same system (the measure of the separation efficiency of the two metal ions), $\Delta(\Delta G_{ex})_{Am/Eu}$, (eq. 3).

$$\Delta(\Delta E_{cf,m})_{Am/Eu} = E(Am\text{-}L)_m - E(Eu\text{-}L)_m - E(Am^{3+})_m + E(Eu^{3+})_m \quad (1)$$

$$\Delta(\Delta G_{part})_{Am/Eu} = G(Am\text{-}L)_{org} - G(Eu\text{-}L)_{org} - G(Am\text{-}L)_{aq} + G(Eu\text{-}L)_{aq} \quad (2)$$

$$\Delta(\Delta G_{ex})_{Am/Eu} = \Delta(\Delta G_{cf})_{Am/Eu} + \Delta(\Delta G_{part})_{Am/Eu} \quad (3)$$

Though the $\Delta(\Delta E_{cf})_{Am/Eu}$ values calculated with the use of B3LYP and PBE functionals are quite different, the small $\Delta(\Delta E_{cf,aq})_{Am/Eu}$ and $\Delta(\Delta G_{cf,aq})_{Am/Eu}$ values (Table 2) point to similar stabilities in water of the $[M(TEDGA)_3]^{3+}$ complexes of Am and Eu. The other quantity which affects the Am/Eu separation – the difference of free energies of liquid-liquid partition of the Am and Eu complexes, which

depends on the balance of hydrophilic and lipophilic properties of the complexes[8] – is also small, therefore $\Delta(\Delta G_{ex})_{Am/Eu}$ is close to 0.

**Table 2** Differences in formation energies, $\Delta(\Delta E_{cf})_{Am/Eu}$, and free energies, $\Delta(\Delta G_{cf})_{Am/Eu}$, of Am and Eu $[M(TEDGA)_3]^{3+}$ complexes; in free energies of their partition ($H_2O \rightarrow TCE$), $\Delta(\Delta G_{part})_{Am/Eu}$, and of extraction of the ions, $\Delta(\Delta G_{ex})_{Am/Eu}$, kJ/mol. Solvent effects accounted for by using COSMO method.

| functional | medium | $\Delta(\Delta E_{cf})$ | $\Delta(\Delta G_{cf})$ | $\Delta(\Delta G_{part})$ | $\Delta(\Delta G_{ex})$ |
|---|---|---|---|---|---|
| B3LYP | gas | +163.4 | – | – | – |
| | $H_2O$ | –2.1 | – | – | – |
| PBE | gas | +104.1 | – | – | – |
| | $H_2O$ | +9.4 | +2.1 | –0.8 | +1.3 |

The resulting conclusion on poor selectivity of diglycolamide ligands in Am/Eu separation is in agreement with the experiments carried out in the TODGA extraction sytems.[10] It should be mentioned, however, that the exact numerical values of the calculated thermodynamic quantities are of little relevance in this discussion because even a simple change of the substrates in the aqueous-phase reaction: nonahydrates $[M(OH_2)_9]^{3+}$ to nitrate complexes $[M(NO_3)(H_2O)_7]^{2+}$; occurring in $HNO_3$ solutions changes the calculated $\Delta(\Delta G_{cf,aq})_{Am/Eu}$ values by a few kcal/mol.[28,38] Unfortunately, more detailed analysis of this question, even qualitative, is not possible at the moment because of mutually incompatible $\Delta G$ values of $[M(NO_3)(H_2O)_7]^{2+}$ formation, reported in the papers referred to above. Also the model assumption on the same degree of outer-sphere association of $[M(TEDGA)_3]^{3+}$ with $NO_3^-$ ions may appear not fully justified.

On the other hand, the large positive $\Delta(\Delta E_{cf,g})_{Am/Eu}$ values (Table 2) show that in the gas phase the $[Eu(TEDGA)_3]^{3+}$ complex is much more strongly bound than its Am counterpart. This can be explained in terms of the stronger electrostatic attraction of negatively charged donor atoms of the ligand by the smaller $Eu^{3+}$ than by somewhat larger $Am^{3+}$ cation of a smaller partial charge (Table 3). The great difference between the $\Delta(\Delta E_{cf,aq})_{Am/Eu}$ and $\Delta(\Delta E_{cf,g})_{Am/Eu}$ values stems from the fact that the complex formation in the aqueous solution requires total dehydration of the nona-aqua metal ions, and that the dehydration energies (also greater for $Eu^{3+}$) must be substracted from the corresponding formation energies (eq. 1). Assuming that the differences between the energies of hydration of the $Eu^{3+}$ and $Am^{3+}$ ions and between the energies of electrostatic attraction of these ions with the ligand are roughly equivalent,[8] we conclude that the $\Delta(\Delta E_{cf,aq})_{Am/Eu}$ value reflects predominantly the difference in covalent contributions to the energies of the metal-ligand bonds in the complexes.

In order to analyze the bond character in the $[Am(TEDGA)_3]^{3+}$ and $[Eu(TEDGA)_3]^{3+}$ complexes we studied their electronic structure in terms of partial charges, bond indices, and topological properties of electron density.

**Charge distribution analysis**

To characterize the covalency of ligand-to-metal bonds in the

complexes we have arbitrarily distinguished three fragments of the TEDGA ligand: the central ethereal, $-CH_2-O_{eth}-CH_2-$, and two lateral alkylamide groups, $(C_2H_5)_2N(C=O_{am})-$, and then computed the shifts of electron density from each fragment on the central metal ions. Such an approach is useful for better understanding the character of donating ability of polydentate ligands with donor atoms of different elements or of the same but of different properties as is the case of TEDGA with amide and ethereal oxygens. In our opinion, the partial charges on the central metal and on the donor atoms only are not sufficiently informative in this respect.

Table 3 presents the average charges on certain ligand atoms, ligand fragments, and on the metal ions in the $[M(TEDGA)_3]^{3+}$ complexes, calculated using NPA, Mulliken's and QTAIM methods. Full data for all the atoms are given in Tables S1, S2 and S4†. The partial charges on the atoms depend on the computational method used, nevertheless, all the methods show a significant transfer of electron density from the coordinated TEDGA ligands on the central metal ions, which reduces their +3 formal charge. The greater shifts on the $Am^{III}$ than on the $Eu^{III}$ cation point to greater covalencies of the Am–O than of the corresponding Eu–O bonds. The total shifts from the three TEDGA ligands are somewhat smaller than those from the two BTBP ligands in $[M(C2-BTBP)_2]^{2+}$; the corresponding partial charges on the Am/Eu atoms, calculated by the same methods being equal to 1.95/2.10, 1.87/1.94, and 2.09/2.19 a.u., respectively.[9] This shows that the TEDGA complexes of both metals are somewhat less covalent than their BTBP counterparts.

All the computational methods used indicate the enhancement of the electron density on the donor oxygen atoms (both amide and etheral), and its decrease on the amide nitrogens and on the hydrocarbon groups in the coordinated TEDGA ligands. The partial charges on the TEDGA donor atoms in the complexes, more negative than those in the free ligand (Table 3), are due to polarization of the coordinated ligands by the central metal cations, stronger by $Eu^{III}$ – the ion somewhat smaller and of a higher partial charge than $Am^{III}$. Perhaps therefore the partial charges on the different donor atoms (N and O) in the BTBP and TEDGA complexes are very close to one another in all the Am and Eu complexes studied, irrespectively of the electron shift values.

The shifts of electron density on the metal ions from the two kinds of TEDGA fragments (related to one donor oxygen atom), $\Delta q_{amide}$ and $\Delta q_{etheral}$, are not very large (Table 3). They are smaller than those from the C2-BTBP fragments (equal to $0.08 \div 0.16$ a.u. in relation to one donor nitrogen atom),[9] and a little bit greater than that from one hard $H_2O$ ligand in nonahydrates (Table S8†). This shows that the

covalent character of the M–O bonds in the complexes is rather small. Unfortunately, each method used in this work led to different relative values of these shifts. The calculations by Mulliken method resulted in significantly greater shift from the alkylamide than from the ethereal fragment, pointing to a greater covalency of the $M–O_{am}$ than of the $M–O_{eth}$ bonds, in agreement with the different lengths of these bonds (Table 1). The conclusion on the significant covalency of $M–O_{am}$ bonds in the TEDGA (TODGA) complexes seems to correspond to that by Roy *et al*. in respect to actinide $DTPA^{5-}$ complexes, where the ligand carboxylic „oxygen atoms provide unexpected covalency to provide additional stabilization of the actinide molecule".[7]

On the contrary, the NPA and QTAIM calculated electron density shifts from the amide and ethereal TEDGA fragments, close to one another, are incompatible with the M–O bond lengths. We consider this disagreement an artefact; the reason of this inconsistency being most probably our arbitrary attribution of the electron density shift from the ethereal $CH_2$ groups entirely to the $O_{eth}$ atom.[39] In fact, these boundary groups probably shift their electron densities to both donors, $O_{eth}$ and $O_{am}$, which would significantly increase the calculated $\Delta q_{am}$ values and decrease the $\Delta q_{eth}$ ones. The resulting shift of electron density to the $M^{3+}$ ion from each alkylamide moiety, significantly greater than that from the ethereal group, allows us to suppose that, contrary to the common opinion,[40-49] the amide oxygen atoms, or rather whole alkylamide groups in a molecule make it not hard but rather a soft base. In contrast, the ethereal groups donating less electron density make the molecule a hard base. Using the terminology of a new approach of „local softness and hardness"[50] we state that the amide oxygen atoms are relatively soft, while the ethereal oxygen atoms are hard.

To support the above conclusion we calculated the hardness of TEDGA and of some other ligands (Table S9†). Chemical hardness of the ligands and of the metal ions studied was calculated using the formula $\eta = (IP – EA)/2$, where IP and EA denote the ionization energy ($IP_{1st}$ for neutral molecules and $IP_{4th}$ for the $M^{3+}$ cations) and electron affinity, respectively, of the species.[51] The optimized structures of the ligands were used to calculate their IP and EA values. The ionization energies of the heavy metal ions were calculated both without and with inclusion of spin-orbit coupling (one-component and two-component ZORA, respectively). The calculated values are given in Table S9†. One can see that $Am^{3+}$ is really a softer acid than $Eu^{3+}$, as well as C2-BTBP ($\eta = 3.36$ eV) is a softer base than TEDGA ($\eta = 4.43$ eV[52]), but the differences are rather small. This confirms the conclusion that the amide oxygen

**Table 3** Average partial charges (a.u.) on selected atoms (groups of atoms) in the $[ML_3]^{3+}$ complexes, (M = Am and Eu, L = TEDGA) and in free TEDGA molecule, calculated using NPA, Mulliken's and QTAIM methods, and the differences between the charges on the corresponding fragments (amide and ethereal) of TEDGA ligand in the given complex and in free ligand molecule, $\Delta q_{amide}$ and $\Delta q_{ethereal}$

| method | compound | M | $O_{am}$ | $C_{am}$ | N | $C_2H_5$ | $O_{eth}$ | $(CH_2)_{eth}$ | amide | etheral | $\Delta q_{amide}$ | $\Delta q_{ethereal}$ |
|--------|----------|---|------|------|---|--------|-------|----------|-------|---------|---------|---------|
| NPA | $[AmL_3]^{3+}$ | 1.99 | –0.698 | 0.664 | –0.315 | 0.257 | –0.515 | 0.261 | 0.165 | 0.007 | 0.11 | 0.11 |
| | $[EuL_3]^{3+}$ | 2.15 | –0.721 | 0.663 | –0.315 | 0.258 | –0.525 | 0.263 | 0.141 | 0.001 | 0.09 | 0.10 |
| | L | - | –0.592 | 0.646 | –0.394 | 0.196 | –0.457 | 0.176 | 0.052 | –0.103 | - | - |
| Mulliken | $[AmL_3]^{3+}$ | 1.98 | –0.638 | 0.522 | –0.295 | 0.280 | –0.575 | 0.310 | 0.149 | 0.045 | 0.14 | 0.07 |
| | $[EuL_3]^{3+}$ | 2.03 | –0.651 | 0.531 | –0.291 | 0.279 | –0.579 | 0.305 | 0.147 | 0.031 | 0.14 | 0.05 |
| | L | - | –0.554 | 0.519 | –0.333 | 0.189 | –0.484 | 0.231 | 0.010 | –0.022 | - | - |
| QTAIM | $[AmL_3]^{3+}$ | 2.30 | –1.141 | 1.269 | –0.973 | 0.457 | –1.010 | 0.551 | 0.069 | 0.093 | 0.07 | 0.09 |
| | $[EuL_3]^{3+}$ | 2.32 | –1.147 | 1.270 | –0.975 | 0.458 | –1.013 | 0.554 | 0.064 | 0.095 | 0.07 | 0.09 |
| | L | - | –1.094 | 1.309 | –0.977 | 0.379 | –0.956 | 0.482 | –0.004 | 0.008 | - | - |

atoms make the TEDGA molecule relatively soft. It is worth mentioning that this conclusion may be helpful for proper interpretation of numerous experimental and theoretical results. For example, high ability to coordinate $Am^{III}$ and $Eu^{III}$ ions by amide oxygen atoms in 2,9-diamide-1,10-phenanthroline ligand, greater than that by ketone atoms in 2,9-diketone-1,10-phenantroline, reported by Mariani *et al.*,[47] correlates with the greater softness of amides than ketones (Table S9†). Also, the more negative formation energies of $Am^{III}/Eu^{III}$ complexes with pyridine-bis(alkyl-aryl)amide ligands than of those with pyridine-bis(dialkyl)amide ligands ("anomalous aryl strengthening"), calculated by Ustynyuk *et al.*,[48] can perhaps be explained as due to a greater shift of electron density to the metal ions form the arylamide moieties, *i.e.* to somewhat greater softness of arylamide ligands. Our hypothesis of relative softness of ligands with donor carbonyl groups (of amide but also of carboxylic moieties) provides a simple explanation for more covalent Am–O than Eu–O bonds in 2,9-dicarboxyl-1,10-phenanthroline complexes, which was concluded from the QM calculations by Manna and Ghanty.[45] In view of that, we consider unjustified their original conclusion that "the presence of softer nitrogen atoms in the Phen moiety ... has a profound influence in changing the soft nature of the actinide ion, which in turn binds with the hard oxygen atoms in a stronger way".[45] However, because both $An^{III}$ and $Ln^{III}$ ions are rather hard acids, still softer di- and triamide ligands become less efficient bases in their complex formation and solvent extraction than harder TODGA, as observed by Sasaki *et al.*[46]

### Bond strength estimation

Two types of methods were used to evaluate M–O bond orders and bond strength in the complexes: (i) methods based on the Natural Atomic Orbitals (NAO); *i.e.* Wiberg bond index (WBI) and the overlap-weighted NAO (NAO, Table 4), and (ii) methods based on the topology of electron density in the molecule, in particular in the bond critical points (Bader's QTAIM analysis, Table 5).

The small WBI values (Table 4) indicate strong ionic character of all the M–O bonds, with a small covalent contribution. All these values we have calculated for single $M–O_{am}$ and $M–O_{eth}$ bonds are significantly lower than the corresponding values calculated by Shi *et al.*,[28] for the respective $[M(TODGA)_2]^{3+}$ complexes (M=Am/Eu), but these differences may result from the fictitious coordination number, CN=6, ascribed[28] to the central metal atoms in the $[ML_2]^{3+}$ complexes, which would make the M–L bonds seemingly stronger and shorter than those with the real CN=9. In fact, also the $M–O_{am}$ and $M–O_{eth}$ distances calculated[28] for $[ML_2]^{3+}$ are shorter than those reported in the present paper (Table 1). The lower WBI indices of Am–O than of the corresponding Eu–O bonds in $[M(TEDGA)_3]^{3+}$ (Table 4) show that the Am–O bonds are more covalent than the corresponding Eu–O bonds, in contrast to the much more negative total energy of the Eu complex formation, calculated in the gas phase (Table 2). The same conclusion can be drawn from the analysis of overlap-weighted NAO indices.

**Table 4** Average Wiberg bond indices (WBI) and overlap-weighted NAO indices (NAO) of the $M–O_{am}$ and $M–O_{eth}$ bonds in the Am and Eu $[M(TEDGA)_3]^{3+}$ complexes

| M–L | Am | | Eu | |
|---|---|---|---|---|
| | WBI | NAO | WBI | NAO |
| $M–O_{am}$ | 0.23 | 0.26 | 0.19 | 0.23 |
| $M–O_{eth}$ | 0.13 | 0.17 | 0.10 | 0.13 |
| Total | 1.99 | 2.09 | 1.67 | 2.27 |

**Table 5** Average values of selected QTAIM parameters of M–O bonds in the $[M(TEDGA)_3]^{3+}$ complexes: electron density at BCP, $\rho_b$; its Laplacian, $\triangledown^2\rho_b$, bond ellipticity, $\varepsilon_b$; ion/cov parameter, and bonding radius, i.e. the distance from the metal atom to BCP, $R_b$.

| bond | $\rho_b$ | $\triangledown^2\rho_b$ | $\varepsilon_b$ | ion/cov | $R_b$ (Å) |
|---|---|---|---|---|---|
| $Am–O_{am}$ | 0.050 | 0.21 | 0.054 | –0.18 | 1.34 |
| $Am–O_{eth}$ | 0.031 | 0.14 | 0.055 | –0.16 | 1.44 |
| $Eu–O_{am}$ | 0.048 | 0.20 | 0.024 | –0.19 | 1.29 |
| $Eu–O_{eth}$ | 0.028 | 0.17 | 0.045 | –0.16 | 1.39 |

The Wiberg indices also allow us to conclude that the M–O bonds in $[M(TEDGA)_3]^{3+}$ are somewhat less covalent than M–N bonds in the corresponding BTBP complexes, for which the WBI values are in the ranges of 0.20÷0.22 in $Am(C2-BTBP)_2]^{3+}$ and 0.15÷0.18 in $Eu(C2-BTBP)_2]^{3+}$.[9] In contrast, the greater overlap-weighted NAO indices for the TEDGA than C2-BTBP[9] complexes point in the opposite direction. This inconsistency requires further study.

Detailed analysis of metal-ligand interactions was also conducted using QTAIM method. The main indicator of a chemical bond covalency is here the electron density, $\rho_b$, at the bond critical point, BCP (the point on the path between two bonded atoms, where $\rho_b$ reaches its maximum in all directions except the bond path). Table 5 shows that the $\rho_b$ values of all corresponding M–O bonds are a little larger in the Am complex than in its Eu analogue, *i.e.* the bonds in the former are more covalent. Also the $M–O_{am}$ bonds are more covalent than the $M–O_{eth}$ ones. The same conclusions on the relative covalency of the Am–O/Eu–O and $M–O_{am}/M–O_{eth}$ bonds in both TEDGA complexes stem from the analysis of Laplacian values at BCPs. The positive signs of $\triangledown^2\rho_b$ show dominant closed-shell non-covalent interactions between M and O. Very similar relationships have been reported for the pair of BTBP complexes of Am and Eu.[9]

The ion/cov parameter, derived from the eigenvalues of the electron density Hessian, has been proposed as another measure of bond covalency.[24] Its value is slightly smaller for all corresponding bonds in the Am complex than in its Eu counterpart, which again indicates slightly larger covalency of the Am–O than Eu–O bonds (though both are mainly ionic), and smaller covalency of the $M–O_{eth}$ bonds in both complexes. This remains in good agreement with the results of the other calculations, reported above. Another parameter derived from the Hessian of the electron density, the bond ellipticity, is very small in all cases, indicating predominantly sigma-type character of the bonds between oxygen lone pairs and both central metal ions. The analysis of the bonding radii shows that the BCPs in the M–O bonds lie near the centres of the bonds, slightly shifted toward the oxygen atom, and that the ionic radius of $Am^{III}$ is slightly larger than that of $Eu^{III}$, in accordance with the results of other calculations.[34,35] In general, the comparison of the QTAIM results for the two pairs of Am/Eu complexes – $[M(TEDGA)_3]^{3+}$ and

[M(C2-BTBP)$_2$]$^{3+}$ – leads to the conclusions which are similar to those resulting from the other theoretical methods.

In order to better understand the origin of the greater covalency of the Am–O than Eu–O bonds in the TODGA (TEDGA) complexes, we studied the effect of electronic structures of the metal ions (as the acceptors of electron density donated from the TEDGA ligands) on the stabilization energy of the complexes. In particular, the contributions from the metal atomic orbitals (AOs) were examined.

### Analysis of atomic orbitals

Natural Population Analysis makes it possible to evaluate the distribution of the electron density on the atomic orbitals of the central metal ions in the complexes. It has been shown that three kinds of valence metal orbitals, *d*, *s*, and *f*, are important electron acceptors in the Am/Eu BTBP complexes, with the decisive role of the 6*d*(Am) orbitals which accept significantly greater electron density from the N-donor ligands than the 5*d*(Eu) orbitals do.[8,9] Table 6 shows a very similar picture for [M(TEDGA)$_3$]$^{3+}$ complexes, which emphasizes the role of the 6*d*(Am) orbitals in the formation of complexes with O-donor ligands as well. Charge transfer from the TEDGA ligand to the central Am ion is larger than that to Eu (even after summation of the occupations of the *d*-type valence and Rydberg's orbitals in the Eu complex). The populations on the Eu/Am 4*f*/5*f* and 6*s*/7*s* valence orbitals are only slightly greater than the nominal values (0 and 6, respectively), so the *f* and *s* orbitals play rather insignificant role in the metal-ligand interactions. Such distribution of the electron density on the atomic orbitals of the central metal ions is very similar to that found in the BTBP complexes[9], which again confirms the conclusion on the relative softness of the diglycolamide ligands.

A more detailed analysis of the role of individual metal AOs in metal-ligand bonding in TEDGA complexes has been performed with the use of the Second Order Perturbation Theory (SOPT, implemented in the NBO package).[22]

Stabilization energy, $\Delta E_{da}^{(2)}$, of donor-acceptor pairs of natural bonding orbitals (NBOs), that contributes to covalency of M–L bonds, considered as second-order perturbation, is proportional to the square of the Fock matrix element and inversely proportional to the difference between energies of acceptor and donor orbitals.[53]

$$\Delta E_{da}^{(2)} = -q_d \frac{|F_{da}|^2}{E_a - E_d} \qquad (4)$$

where $q_d$ is the occupancy of the donor orbital ($q_d \approx 2$); $E_a$ and $E_d$ are the energies of the acceptor and donor NBOs, respectively; and $F_{da}$ - an off diagonal element of Fock matrix. At Mulliken approximation $|F_{da}| \sim S_{da}$, where $S_{da}$ is the overlap integral.

Neidig et al.[54] distinguish two kinds of covalency: (i) overlap driven, *i.e.* classical – related to overlap integral; and (ii) near degeneracy driven – related to proximity of the energies of the acceptor and donor orbitals. In the SOPT analysis, the parameters relevant to this concept are the Fock matrix elements and the energy gaps, respectively.

**Table 6** NPA analysis of charge distribution on some atomic orbitals (AOs) of Am and Eu ions in the [M(TEDGA)$_3$]$^{3+}$ complexes

| complex | Partial charges on AOs of Am$^{3+}$ and Eu$^{3+}$ |
|---|---|
| [AmL$_3$]$^{3+}$ | [core] 7s(0.14) 5f(6.13) 6d(0.71) 7p(0.01) |
| [EuL$_3$]$^{3+}$ | [core] 6s(0.13) 4f(6.07) 5d(0.61) 6p(0.01) 6d( 0.05) |

The values of the energy gaps, Fock matrix elements and stabilization energies have been calculated for each donor-acceptor pair in the complexes studied. Tables S10 and S11 present the hybrid orbitals of greatest stabilization energies in the [Eu(TEDGA)$_3$]$^{3+}$ and [Am(TEDGA)$_3$]$^{3+}$ complexes, as well as their $\Delta E_{da}^{(2)}$, $E_a - E_d$, and $F_{da}$ values related to each pair of the interacting orbitals. The greatest stabilization energy of the [Am(TEDGA)$_3$]$^{3+}$ complex results from the interactions of six hybrid LP* NBOs of the pure *d* character and the *d-f* hybrids (4÷18% *f*) of Am with the *s-p* LP hybrids on the O$_{am}$ and O$_{eth}$ atoms, each contributing over 5 kcal/mol. The interactions of four LP* NBOs of the pure *s* character with the *s-p* LP hybrids contribute *ca*. 3.5÷4 kcal/mol each. As expected from these results, the interactions of the LP* NBOs with the LP-O$_{am}$ hybrids contribute more to the stabilization energy than those with the LP-O$_{eth}$ hybrids. The greatest stabilization energy of the [Eu(TEDGA)$_3$]$^{3+}$ complex results from the interactions of six hybrid LP* NBOs (of the pure and almost pure *d* character, ~1% *f*, an also of the pure *s* character) of Eu with the *s-p* LP hybrids on the O$_{am}$ and O$_{eth}$ atoms, over 5 kcal/mol each. The total stabilization energy for [Am(TEDGA)$_3$]$^{3+}$ is greater than that for its Eu counterpart, and the contribution from the interactions of the LP* NBOs with the LP-O$_{eth}$ hybrids in both complexes is rather low, in accordance with the previous results.

The analysis of the $F_{da}$ and $E_a - E_d$ values related to the most stabilizing interactions allows us to conclude that the covalency of the M–O$_{am}$ bonds in both complexes is mainly overlap driven, while that of the M–O$_{eth}$ bonds, of smaller $F_{da}$ values is rather near degeneracy driven. However, a caveat needs to be issued at this point that both orbital energy differences and Fock matrix elements (probably the former more than the latter) are likely to be affected by spin-orbit coupling, so it is possible that the results of the analysis of molecular orbitals derived from two-component instead of one-component ZORA calculations would lead to a different conclusion.

The results of SOPT analysis confirm the NPA conclusions on the crucial role of the valence *d* orbitals of the Am and Eu cations in the stability of the TEDGA complexes, and on much smaller contribution from the valence *s* and *f* metal orbitals. The greater occupancy of 6*d*(Am) than of 5*d*(Eu) orbital in the [M(TEDGA)$_3$]$^{3+}$ complexes is due to the greater radial extent of the former, as is the case of BTBP complexes.[9]

The question of which valence orbitals of actinides are responsible for more covalent character of their metal-ligand bonds than in the case of lanthanides is quite old. Some authors (for example[55,56]) still consider *a priori* the 5*f* orbitals of actinides to be the crucial ones in this respect. However, various QM studies point to various actinide orbitals participating in the metal-ligand bonding.[9,30,31,57,58] One can conclude that the answer to the above question depends on a given metal ion and on a given ligand. Kaltsoyannis[57,58] studied Mulliken populations and spin densities on the central metal ions in cyclopentadienyl complexes of actinides(III,IV). The contribution from the actinide 6*d* orbitals to the bonding MOs decreased across

the actinide series, and that from 5*f* orbitals significantly increased (in parallel to the decrease in their energy), to reach the maximum at americium. This effect, leading to the decisive role of 5*f* orbitals in the covalency of Am–C bonds, has been attributed[57,58] to the fortuitous energy match of the 5*f*(Am) and ligands donor orbitals, but without any significant overlap (near degeneracy driven covalency). In contrast to that, the decisive role of *d* orbitals in the covalency of M–O bonds in the Am/Eu TEDGA complexes, concluded in the present paper, is mainly (but not entirely) due to the overlap driven covalency. It should also be mentioned at this point that in the case of relatively small effects, different analytical tools often yield different conclusions,[58] so it is advisable to use a variety of analytical techniques.

In general, the results of bonding analysis by all the QM methods we have used - based on Natural Atomic Orbitals and on the topology of electron density in isolated molecules - agree with the differences in the energies of complex formation calculated in water (COSMO + hydrated metal ions as the substrates) rather than with the differences in total bonding energies of the isolated molecules. This conclusion remains in agreement with the recent observations by Kaltsoyannis and co-workers who found strong positive correlation of QTAIM parameters of selected bonds in certain actinide compounds with the orbital mixing energy term or with the bond stretching wavenumber, while their correlation with the total bonding energy is very poor.[59,60] Therefore, we believe that our results extend that observation, and allow us to state that the Mulliken population analysis, QTAIM topological parameters, and SOPT stabilization energy, as well as Wiberg and overlap-weighted NAO indices are the tools for analyzing covalency rather than the total bond strength in heavy metal compounds.

## Conclusions

Cationic complexes of Eu$^{III}$ and Am$^{III}$, [M(TEDGA)$_3$]$^{3+}$, are nearly equally stabilized by weak charge transfer from ligand donor orbitals to empty valence hybrid orbitals (of mainly d-character) of the metal ions. Small differences in the computed energies and Gibbs free energies of [M(TEDGA)$_3$]$^{3+}$ formation (in water) by the metal ions, and in the free energies of transfer (partition) of the complexes from water to an organic phase confirm poor selectivity of the TODGA ligand in Am/Eu complexation and solvent extraction separation, experimentally observed. However, neither the differences of these thermodynamic functions, nor the analysis of M–L bonds in [M(TEDGA)$_3$]$^{3+}$ correspond to the HSAB principle, under a priori assumption on chemical hardness of the oxygen-donor TEDGA ligand. On the contrary, the analysis of charge distribution in the separate fragments of the complex molecules, showing the significant charge transfer to the metal ions, especially through the amide oxygens, as well as the calculated chemical hardness of the ligands studied, lead to the conclusion that the TEDGA molecule is not hard as expected, but relatively soft; only slightly harder than BTBP. The covalency of the Am–O bonds is somewhat greater than that of Eu–O ones, though the difference is smaller than in the case of the M–N bonds in the [M(C2-BTBP)$_2$]$^{3+}$ complexes. This justifies the conclusion on the relative softness of the TEDGA (TODGA)

ligand, somewhat smaller than the softness of BTBP.

The conclusion on slightly greater covalency of the Am–O than Eu–O bonds in [M(TEDGA)$_3$]$^{3+}$ corresponds to somewhat more negative formation energy of the Am complex in water (B3LYP, Table 2), but not in the gas phase. This apparent contradiction is due to the fact that the energy calculated for isolated molecules contains the component of electrostatic attraction between negatively charged ligand donor atoms and the metal cations, greater for the smaller Eu$^{III}$ than larger Am$^{III}$ cation. This component vanishes (at least to a large extent) when calculating the formation energy in water, with the explicitly hydrated metal ions as the substrates, because the different energy of dehydration of the metal ions compensates the effect of their different electrostatic attraction of the ligand. Therefore, the formation energies in water correlate with the covalent and not ionic (electrostatic) component of the total energy of metal-ligand bonds, in spite of their predominantly ionic character. The agreement between the values of formation energy calculated in water and the results of bonding analysis based on the topology of electron density in the isolated molecule allows us to conclude that the theoretical methods used: Mulliken population analysis, bond strength indices (NAO), QTAIM topological parameters, and SOPT stabilization energy are the tools for analyzing covalency rather than the total bond strength.

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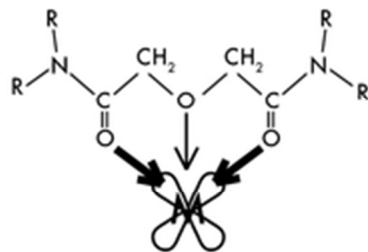
Charge transfer from ligand to valence hybrid (mainly d) metal orbitals nearly equally stabilizes cationic $Eu^{III}$ and $Am^{III}$ TODGA complexes.

39x19mm (300 x 300 DPI)