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Metal Polycations

A Tetrapositive Metal Ion in the Gas Phase: Thorium(IV) Coordinated by Neutral Tridentate Ligands[**]

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Multiply charged metal cations play important roles in solid-state and solution chemistry. Studies on isolated multiply charged cations in the gas phase have provided critical information about their structure, bonding, and reactivity under solvent-free conditions.[1] Several approaches have been employed to produce ligand-supported multiply charged cations in the gas phase, including electron ionization, photoionization, electrospray ionization (ESI), and charge stripping and transfer.[2] Highly charged species usually form charge-reduction products through a Coulomb explosion, which is increasingly favored when the first ionization energy of the ligand lies substantially below the higher ionization energies (2nd, 3rd, or higher) of the metal.[2,3] Dications are the most commonly observed multiply charged cations in the gas phase.[4] A few diatomic and triatomic transition metal and actinide trications have been produced by ion and laser sputtering and charge stripping.[5–7] Other trications of lanthanide, transition metal, and main group elements with the third ionization energies up to approximately 30 eV were produced in the gas phase by ESI and electron ionization using aprotic ligands.[8–10] Stabilization of trications with protic ligands, such as water, requires some twenty or more ligands such that the highly charged metal center is solvated in a nanodroplet.[11,12] Diacetone alcohol is a protic ligand that forms metal trication complexes in the gas phase, presumably through coordination to the carbonyl group.[13] Large ligands such as peptides and sucrose can also form stable triply charged metal-containing species.[14,15]

In contrast to trications, reports of gas-phase metal tetracation complexes are rare. Diatomic NbO^{4+} and TaO^{4+} have been reported.[7] Theoretical calculations suggested metastable $Zr(CH_3CN)^{4+}$ might be observed, a hypothesis that has yet to be demonstrated.[16] To the best of our knowledge, there have been no reported observations of metal tetracation coordination complexes in the gas phase.

In a quest for multiply charged actinides in the gas phase by ESI,[17] we report herein the $Th(L)_3^{4+}$ tetracation, where L = tetramethyl-3-oxaglutaramide (TMOGA; structure shown in Figure 1; also referred to as TMDGA, N,N,N',N'-tetramethyl diglycolamide). TMOGA is the smallest homologue of diglycolamide extractants that exhibit a particular propensity for separation of trivalent lanthanides and actinides.[18] The structures of several diglycolamide-supported lanthanide and actinide complexes have been reported.[19–21] Thorium has a low fourth ionization energy, 28.8 eV,[22] which is below the third ionization energies of transition metals for which gas-phase ligated trications have been observed.[9] The expected strong interaction of TMOGA with Th^{4+} offers the possibility of stabilization of Th^{4+}/TMOGA complexes in the gas phase.

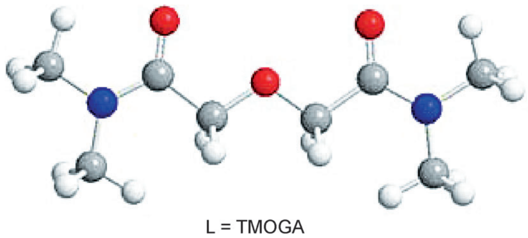

Figure 1. Structure of the TMOGA ligand (O red; N blue; C gray; H light gray).

The positive-mode ESI mass spectrum of a 1:1 $Th(ClO_4)_4$/TMOGA mixture in acetonitrile (shown in Figure 2) is dominated by intense peaks at m/z 198.8 and 298.3. The former is assigned to the $Th(L)_3^{4+}$ complex, the exact m/z of which is 199.1 (the difference between m/z 198.8 and 199.1 is within the instrumental accuracy—see Supporting Information, Table S1). The presence of 24 carbon atoms in the complex results in a 26 % relative abundance isotopomer with one ^{13}C isotope at one higher mass unit. This ^{13}C peak appears as a distinct feature at m/z 0.25 above the most intense peak, as is seen in the inset in Figure 2; the splitting of m/z 0.25 confirms the charge of 4+ and the assignment as $Th(L)_3^{4+}$. Collision-induced dissociation (CID) of the $Th(L)_3^{4+}$ complex

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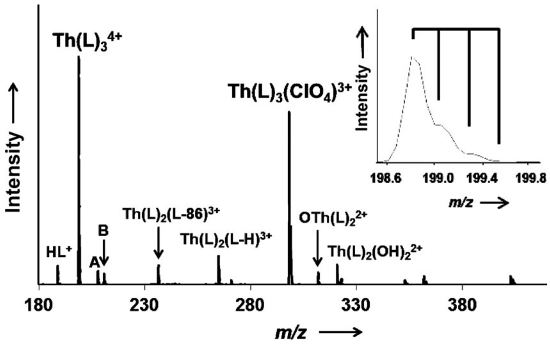

Figure 2. ESI mass spectrum of $Th(ClO_4)_4$ and TMOGA (L) mixtures in acetonitrile. $A = Ca(L)_2^{2+}$; $B = Na(L)^+$. The partially resolved isotopic profile, owing to the presence of ^{13}C-containing isotopomers for $Th(L)_3^{4+}$, is shown in the inset and reveals a peak spacing of m/z 0.25 and thus an ion charge of 4+.

produced peaks at m/z 236.5 and 208.2 with $^{12}C/^{13}C$ splittings of 0.33 indicating charges of 3+ (Figure S1); these are assigned as $Th(L)_2(L\text{-}86)^{3+}$ and $Th(L)_2(OH)^{3+}$, where L-86 represents a TMOGA ligand that has lost a fragment of mass 86. Formation of trications upon CID supports the assignment of tetrapositive $Th(L)_3^{4+}$. The isotopic profile and splitting of the m/z 298.3 peak in the parent mass spectrum suggests that it corresponds to $Th(L)_3(ClO_4)^{3+}$. Other trications, as well as dications with moderate intensities, were also apparent in the ESI mass spectrum (Table S1). Sodium and calcium were observed as $Na(L)^+$ and $Ca(L)_2^{2+}$ at m/z 210.9 and 207.9. The $^{12}C/^{13}C$ isotopic splitting for $Ca(L)_2^{2+}$ is 0.5, twice that for the $Th(L)_3^{4+}$ complex.

The $Th(L)_3^{4+}$ peak in Figure 2 is dominant in the spectrum, suggesting this is a particularly stable gas-phase tetracation. To get insights into the structure, bonding, and energetics of this complex, geometry optimizations were carried out using LDA, PBE, and B3LYP functionals. Because these calculations gave similar results, only the geometry optimized at the PBE level is presented herein. The $Th(L)_3^{4+}$ complex is calculated to have C_3 symmetry with Th^{4+} coordinated by three ligands (Figure 3). The calculated Th–$O_{carbonyl}$ distance (2.40 Å) is shorter than that of Th–O_{ether} (2.67 Å), which is close to distances reported for other thorium containing systems.[23] The Th–$O_{carbonyl}$ distance is only slightly longer than a single Th–O bond distance of 2.38 Å, obtained from the estimated single-bond radii of Th and O atoms.[24] Because there are direct interactions between thorium and all three oxygen atoms in each TMOGA, the thorium center in $Th(L)_3^{4+}$ is in ninefold coordination. This twisted tricapped trigonal prismatic (TPP) structure is similar to those of lanthanide and Pu^{IV} solid complexes with the metal center coordinated by three ligands.[20,21] These actinide complexes with nine-coordination TPP geometry are examples of uncommon chiral molecules with 5f-elements.[25] Given the recent interest in chiral materials with 4f-elements,[26] chiral $An(L)_3^{4+}$ complexes might serve as a unit for assembling novel chiral materials with 5f-elements.

Our theoretical studies based on Kohn–Sham MOs, Weinhold's natural bond orbitals (NBOs) and natural localized MOs (NLMOs), Mulliken population analysis, Nalewajski-Mrozek bond orders, and energy decomposition analysis (EDA) indicate that in addition to the ionic interactions between Th and TMOGA, there are direct, albeit weak, donating bonding interactions from the two $O_{carbonyl}$ atoms and the central O_{ether} atoms. As shown in Table S6, the TMOGA ligand has two C–O bonds and two lone-pairs for $O_{carbonyl}$ and O_{ether}, respectively. Upon coordination to a Th^{4+} ion, there are covalent electron donations from the lone pairs to the metal, with the donation from the $O_{carbonyl}$ atoms being larger than from the O_{ether} atom; this is consistent with the calculated bond orders in Table S2. The Kohn–Sham MOs depicted in Table S8 clearly show the orbital interactions between Th and TMOGA. These bonding interactions account for the stability of the tetrapositive ion.

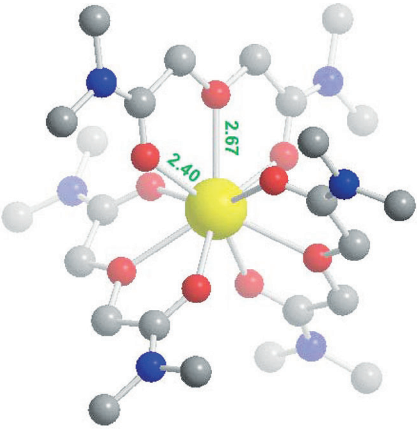

Figure 3. Optimized structure of $Th(L)_3^{4+}$ with C_3 symmetry at DFT/PBE level (bond lengths in Å; O red, N blue, C gray, Th yellow). Hydrogen atoms are omitted for clarity. To provide a 3D perspective, atoms protruding from the plane of the page are in bold; atoms behind the plane are shaded.

Previous CID studies on multiply charged cations showed that they undergo reactions, including reduction to give electron or proton transfer products, charge conserving cleavage by losing a neutral ligand, and reduction by elimination of charged ligand fragments.[9,10] CID of $Th(L)_3^{4+}$ (Figure S1) mainly resulted in $Th(L)_2(L\text{-}86)^{3+}$ (Equation (1)), with minor $Th(L)_2(OH)^{3+}$ (Equation (2)). The $Th(L)_2(L\text{-}86)^{3+}$ cation is formed by losing $(86)^+$, which corresponds to the $(CH_3)_2NC(O)CH_2$ moiety resulting from C–O_{ether} bond cleavage in TMOGA; this is considered the major radiolytic degradation channel of diglycolamides in solution under acid-free conditions.[27] The relatively weak $Th(L)_2(OH)^{3+}$ peak presumably arises from hydrolysis of $Th(L)_3^{4+}$ through the loss of HL^+ under CID condition owing to trace H_2O in the ion trap.[28] In contrast to the CID behavior of ligated metal trications,[9,10] neither $Th(L)_2^{4+}$ nor $Th(L)^{4+}$ was observed, indicating that loss of a neutral ligand does not occur for the tetrapositive complex; charge reduction by ligand cleavage is instead favored.

$$Th(L)_3^{4+} \rightarrow Th(L)_2(L\text{-}86)^{3+} + (86)^+ \qquad (1)$$

$$Th(L)_3^{4+} + H_2O \rightarrow Th(L)_2(OH)^{3+} + (HL)^+ \qquad (2)$$

The present results suggest that three TMOGA ligands are necessary to form a stable gas-phase complex with the Th^{4+} ion, raising the question as to whether the tetracation could be stabilized by two or four TMOGA ligands. In contrast to other metal trication complexes that exhibit a series of compositions with different numbers of ligands,[8,9,13] only $Th(L)_3^{4+}$ was observed when the Th/L ratio in solution was varied from 1:0.2 to 1:10; the highest yield of $Th(L)_3^{4+}$ was obtained for a Th/L ratio close to 1:1. No $Th(L)_3^{4+}$ ion was observed with an insufficient ligand concentration and intense $Na(L)_{1,2}^{+}$ peaks appeared when the ligand concentration was in large excess. The absence of $Th(L)_n^{4+}$ ions for $n=1$, 2, or 4 indicates that three TMOGA ligands are necessary and sufficient to stabilize Th^{4+} ions in the gas phase. The preference for three TMOGA to stabilize Th^{4+} ions can be evaluated from the calculated ligand binding energies for Equation (3), which are listed in Table 1; structural details for $Th(L)_n^{4+}$ ($n=1$–4) are given in Figure S2 and Table S2.

Table 1: Calculated binding energies at the PBE/SR, PBE/SO and B3LYP levels of theory.[a]

	ΔE (PBE/SR)	ΔE (PBE/SO)	ΔE (B3LYP)
$Th(L)_1^{4+}$	−2802	−2807	−2803
$Th(L)_2^{4+}$	−1174	−1176	−1258
$Th(L)_3^{4+}$	−581	−581	−641
$Th(L)_4^{4+}$	−191	−192	−221

[a] Energies in $kJ\,mol^{-1}$. ΔE is the energy for Equation (3). SR = scalar relativistic; SO = spin-orbit.

$$Th(L)_{n-1}^{4+} + L \rightarrow Th(L)_n^{4+} \;\; (n = 1-4) \tag{3}$$

The energy released upon coordination of TMOGA to $Th(L)_{n-1}^{4+}$ ($n=1$–4) decreases from approximately 2800 $kJ\,mol^{-1}$ for $n=1$ to approximately 200 $kJ\,mol^{-1}$ for $n=4$; the $Th{-}O_{carbonyl}$ and $Th{-}O_{ether}$ bond distances concurrently increase. According to our PBE calculations, the $Th(L)_2^{4+}$ complex possesses D_{2d} symmetry (Figure S2) with thorium coordinated by all three oxygen atoms in each TMOGA. The association energy between TMOGA and $Th(L)_2^{4+}$ is about half that between TMOGA and $Th(L)^{4+}$, but it is nonetheless energetically favorable by about 600 $kJ\,mol^{-1}$ to form $Th(L)_3^{4+}$ from $Th(L)_2^{4+}$. The exothermal energy release for the addition of a fourth ligand to $Th(L)_3^{4+}$ is substantially less, at approximately 200 $kJ\,mol^{-1}$. Our calculations show that the optimized Th−O distances in the formally twelve-coordinated $Th(L)_4^{4+}$ (D_2) structure are 2.51 Å, 2.57 Å, and 2.87 Å, respectively, longer than the estimated length of the Th−O single bond (2.38 Å).[24] The EDA results in Table S7 also indicate that with increasing ligation both the bonding energy per TMOGA ligand and the orbital interactions decrease.

Other than $Th(L)_3^{4+}$, $Th(L)_3(ClO_4)^{3+}$ was the only species containing three TMOGA ligands. The recently reported Vis–NIR spectrum of crystalline $Pu^{IV}(L)_3^{4+}$ exhibited similarities to that for this solid dissolved in solution, indicating that the $Pu^{IV}(L)_3^{4+}$ complex exists in solution.[21] Similarly, ligated $Th(L)_3^{4+}$ is likely a solution complex, in accord with the intense $Th(L)_3^{4+}$ peak in the ESI mass spectrum and the appearance of the $Th(L)_3^{4+}{\cdot}ClO_4^{-}$ complex.

ESI of mixed $Th(ClO_4)_4$ and TMOGA in methanol resulted in no $Th(L)_3^{4+}$ but was instead dominated by $Th(L)_3(CH_3O)^{3+}$ and $Th(L)_2(L\text{-}H)^{3+}$, as well as by dications such as $Th(L)_2(CH_3O)_2^{2+}$, $Th(L)_2(OH)(CH_3O)^{2+}$, and $Th(L)_2(CH_3O)(ClO_4)^{2+}$. Most of the thorium containing species had a CH_3O group, indicating that $Th(L)_3^{4+}$ is reduced by methanol during ESI. With the solvent acetonitrile, the yield of $Th(L)_3^{4+}$ ions in the gas phase was greatest when the solution contained the lowest water concentration, 0.1% H_2O. As the water concentration increased, the yield of $Th(L)_3^{4+}$ ions decreased. It is apparently unfavorable to stabilize a tetracation in the presence of water.

In summary, ESI of 1:1 mixtures of $Th(ClO_4)_4$ and ligand TMOGA in acetonitrile resulted in the observation of the TMOGA supported tetracation, $Th(L)_3^{4+}$, in the gas phase. Three TMOGA ligands are necessary to stabilize the tetrapositive thorium ion; no $Th(L)_2^{4+}$ or $Th(L)_4^{4+}$ ions were observed. Theoretical calculations reveal that the $Th(L)_3^{4+}$ complex possesses C_3 symmetry with the thorium coordinated by nine oxygen atoms from three ligands, which forms a chiral twisted TPP geometry with a nine-coordinate thorium center. The Th-L binding energy and bond orders of $Th(L)_n^{4+}$ decrease as the coordination number increases, consistent with the trend of concurrently increasing Th−O distances. The Th−O bonding is mainly electrostatic in nature, but the covalent interactions are not negligible. CID of the $Th(L)_3^{4+}$ complex mainly resulted in a charge decrease to form $Th(L)_2(L\text{-}86)^{3+}$; loss of neutral TMOGA was not observed. The protic ligand methanol stabilized only tri- and dications of ligated thorium. The intensity of the $Th(L)_3^{4+}$ peak diminished as the concentration of water in the acetonitrile solution increased.

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