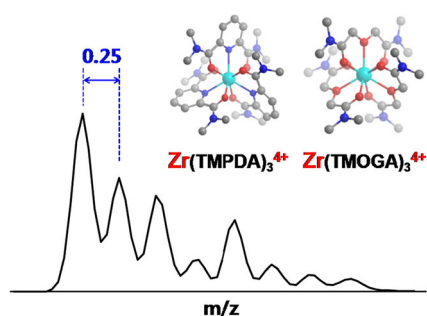CrossMark

RESEARCH ARTICLE

Formation and Characterization of Zr^{4+} Stabilized by Neutral Tridentate Ligands in the Gas Phase

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Abstract. Ligated tetrapositive metal ions are rare gas-phase species which tend to form complexes with lower charges due to the high 4th ionization energies of metals. We report the observation of tetrapositive $Zr(TMPDA)_3^{4+}$ and $Zr(TMOGA)_3^{4+}$ complexes in the gas phase by electrospray ionization of $Zr(ClO_4)_4$/TMPDA and $Zr(ClO_4)_4$/TMOGA mixtures. The Zr^{4+} center in both complexes is coordinated by nine atoms from three neutral diamide ligands forming nine-coordinate twisted tricapped trigonal prismatic geometry on the basis of DFT calculations. Collision-induced dissociation of both complexes resulted in the loss of protonated ligands to form tripositive $Zr(TMPDA)(TMPDA-H)^{3+}$ and $Zr(TMOGA)(TMOGA-H)^{3+}$ products which retain the IV oxidation state of zirconium at the cost of charge reduction from 4+ to 3+ of the whole complexes. The very high 4th ionization energy of zirconium (34.34 eV) makes tetrapositive zirconium complex the most challenging tetracation to be stabilized against charge reduction in the gas phase to date.

Keywords: Multiply charged cation, Zirconium, Pyridinedicarboxamide, Diglycolamide, Gas phase

Introduction

As the most common oxidation state of zirconium, Zr(IV) dominates the chemistry of zirconium complexes in aqueous chemistry. However, due to the high tendency towards hydrolysis, monomeric Zr^{4+} ions are only stable at low concentration ($\sim 10^{-4}$ M) and high acidic condition (pH < 0) while formation of polymeric species such as tetranuclear $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ is favored in other cases [1]. Such hydrolytic character of Zr^{4+} complicates its aqueous chemistry and makes it difficult to probe the properties of simple Zr^{4+} ions under aqueous condition. It has been demonstrated that the chemistry of solution species can be also investigated in the gas phase, the results of which parallel the solution chemistry of metal ions [2–5]. This is particularly important for the

fundamental understanding on the chemical behaviors of multiply charged metal ions. It is well known that electrospray ionization (ESI) is a powerful approach to transfer ligated multiply charged cations into the gas phase [6, 7], but the high charge of metal ions prevents the stabilization of gaseous $[M(L)_n]^{z+}$ ($z > 2$) complexes against charge transfer via Coulomb explosion due to the high ionization energies (IEs) of metal ions [8, 9]. For example, the 3rd ionization energies (IEs) of almost all metals are above 19 eV, higher than the average IEs of typical organic ligands ($\sim$ 8–13 eV) [10]. Despite the difficulties in stabilizing simple tripositive metal complexes, a series of main group, transition metal, lanthanide, and actinide trications supported by simple ligands such as diacetone alcohol (DAA) [11], dimethyl formamide (DMF) [12], dimethyl sulfoxide (DMSO) [12–14], acetonitrile [15–17], peptides [18–20], and diamides [5, 21, 22] have been observed. As for tetrapositive metal complexes, it is extremely difficult to observe them in the gas phase since the 4th IEs of most metals are above 30 eV [10], substantially higher than the IEs of simple organic ligands. To the best of our knowledge, stable gas phase tetrapositive ions are limited to An^{4+} (An = Th, U, Np, and Pu)

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supported by neutral N,N,N′,N′-tetramethyl-3-oxa-diglycolamide (TMOGA) ligands. The 4th IE of Th is 28.8 eV, and those of U, Np, and Pu are estimated to be above 32 eV without exact experimental data [23, 24].

The observation of ligated tetrapositive actinide ions in the gas phase indicates the possibility of stabilizing Zr^{4+} by multidentate diamide ligands, which seems consistent with the remarkable extraction capacity of TROGA (N,N,N′,N′-tetraalkyl-3-oxa-diglycolamide) towards Zr^{4+} in aqueous solution [25–27]. However, the 4th IE of zirconium (34.34 eV) is higher than those of all the actinides studied before [10], and Zr^{4+} shows an extremely high tendency towards hydrolysis [1]. All these properties imply that it is even more challenging to observe quadruply charged zirconium complex in the gas phase. While there is no report on the observation of gas-phase tetrapositive zirconium ions, theoretical calculations suggested that the metastable $Zr(CH_3CN)^{4+}$ ion appears to be a good experimental candidate despite the difficulties on how it can be generated experimentally [28]. In this paper, we report the first observation of gaseous tetrapositive zirconium ion supported by TMPDA (N,N,N′,N′-tetramethylpyridine-2,6-dicarboxamide, Figure 1) and TMOGA ligands. Density functional theory (DFT) calculations were performed to understand the coordination structures of these complexes. Their fragmentation chemistry was investigated by collision-induced dissociation (CID) which provides insights into the chemical properties of ligated Zr^{4+} ions.

Experimental and Theoretical Methods

All the experiments on the gas-phase chemistry of $Zr(TMPDA)_3^{4+}$ and $Zr(TMOGA)_3^{4+}$ were performed on a ThermoScientific (San Jose, CA) LTQ-XL linear ion trap mass spectrometer equipped with an Heated Ion Max electrospray ionization (HESI) source. $Zr(ClO_4)_4$ (500 µM) and TMPDA/ TMOGA (ratios varying from 5:1 to 1:5) mixtures in acetonitrile were prepared for ESI experiments. Both $Zr(TMPDA)_3^{4+}$ and $Zr(TMOGA)_3^{4+}$ ions were most abundant at a mole ratio of 1:3 (metal:ligand). The diluted zirconium solution was prepared from a freshly prepared $Zr(ClO_4)_4$ solution (50 mM, pH = 1). TMPDA and TMOGA ligands were synthesized according to the literature [29, 30]. The MSⁿ CID capabilities of the LTQ/MS allow isolation and excitation of $Zr(TMPDA)_3^{4+}$/$Zr(TMOGA)_3^{4+}$ and ion dissociation is achieved by multiple energetic collisions with the He buffer gas. CID was carried out on both single and multiple isotopomers of $Zr(TMPDA)_3^{4+}$ and Zr $(TMOGA)_3^{4+}$, and only the results from the most intense single isotopomer is presented. In enhanced mode, the instrument has a detection range of
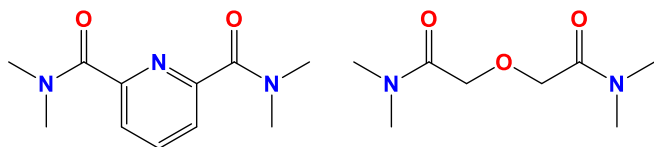
m/z 50~2000 with a mass width (FWHM) of $m/z \sim 0.25$. Mass spectra were recorded and accumulated in the positive polarity mode with the following instrumental parameters: solution flow rate, 10 µL/min; source voltage, 4.50 kV; source current, 1.98 µA; source temperature, 107.18 °C; auxiliary gas flow rate, 10.00 arb; sweep gas flow rate, 4.99 arb; capillary voltage, 30.24 V; capillary temperature, 56.63 °C; tube lens voltage, 50.61 V; multipole 00, 0, and 1 offset, − 2.95, − 8.46 and − 11.89 V; lens 0 and 1, − 7.18 and − 13.04 V; gate, front and back lens, − 80.37, − 8.82, and − 0.40 V; front, center, and back section, − 8.92, − 11.91, and − 6.82 V; and multipole RF amplitude, 396.43 Vpp. The abundances of multiply charged cations strongly depend on the capillary voltage, tube lens voltage and gas flow rate. These parameters were slightly adjusted to maximum the abundances of Zr-bearing complex cations. The normalized collision energies (NCE) were 11 and 7% during CID of $Zr(TMPDA)_3^{4+}$ and $Zr(TMOGA)_3^{4+}$. Increasing the NCE only affected the yield of the fragments while their relative abundances remained the same. High purity nitrogen (99.999%) gas for nebulization and drying in the ESI source and helium (99.999%) used as the collision gas were supplied from the nitrogen and helium cylinders. The pressure inside the ion trap is about 7.5×10^{-6} Torr during all the experiments.

Density functional theory (DFT) calculations of $Zr(TMPDA)_3^{4+}$ and $Zr(TMOGA)_3^{4+}$ were carried out using the Gaussian09 program [31]. The hybrid B3LYP functional was employed in our calculations [32, 33]. The 6-31G(d) basis set was used for H, C, N, and O [34, 35], and the 28 electron core SDD pseudopotential was used for zirconium [36]. All of the geometry parameters were fully optimized, and the harmonic vibrational frequencies were obtained analytically at the optimized structures. Zero-point energy (ZPE) corrections were included in the calculations of relative energies. The natural bond orbital (NBO) analysis was performed on the $Zr(TMPDA)_3^{4+}$ and $Zr(TMOGA)_3^{4+}$ complexes optimized at the B3LYP level of theory [37].
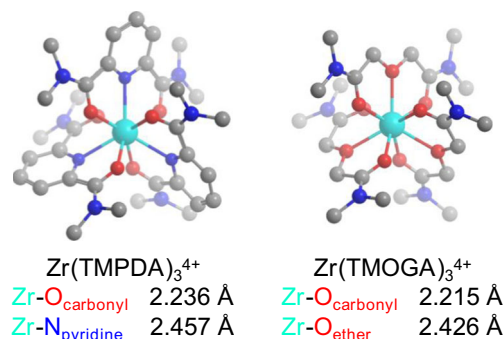
Results and Discussion

The mixture of 1:3 $Zr(ClO_4)_4$ (500 µM) and TMPDA in acetonitrile was prepared for positive polarity mode enhanced ESI. The ESI mass spectrum (Figure 2, top) is dominated by two sets of peaks at m/z 188.32 and 284.08. A series of peaks starting at m/z 188.32 exhibits a splitting of m/z 0.25 between the two neighboring peaks. The overall profile of the peaks as well as the m/z 0.25 interval indicates these peaks should be due to a tetrapositive zirconium complex, $Zr(TMPDA)_3^{4+}$. As shown in Figure 2, the observed isotopic peak profile agrees well with the calculated one, and the presence of a series of satellite peaks above the most intense peak at m/z 188.32 arises from the natural isotopes of zirconium and carbon ($^{12}C/^{13}C$). The observed m/z ratio of 188.32 is also in good agreement with the calculated value of 188.36 for $Zr(TMPDA)_3^{4+}$. In addition to the only tetrapositive zirconium complex

Figure 1. Structures of TMPDA (left) and TMOGA (right)
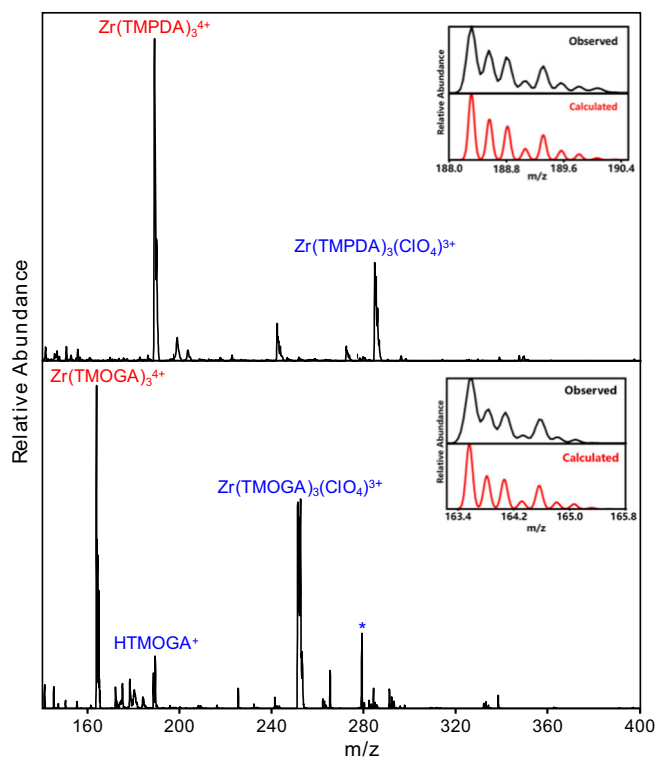
Figure 2. ESI mass spectra of 1:3 Zr (ClO$_4$)$_4$ (500 μM) and TMPDA/TMOGA mixtures in acetonitrile. The asterisk denotes Fe(TMOGA)Cl$^+$. Experimental (black) and calculated (red) mass spectra of Zr(TMPDA)$_3^{4+}$ and Zr(TMOGA)$_3^{4+}$ are shown in the insets. The resolved isotopic profile in each inset reveals a peak splitting of *m/z* 0.25

Zr(TMPDA)$_3^{4+}$	Zr(TMOGA)$_3^{4+}$
Zr-O$_{carbonyl}$ 2.236 Å	Zr-O$_{carbonyl}$ 2.215 Å
Zr-N$_{pyridine}$ 2.457 Å	Zr-O$_{ether}$ 2.426 Å

Figure 3. Optimized structures of Zr(TMPDA)$_3^{4+}$ and Zr(TMOGA)$_3^{4+}$ at the B3LYP level of theory. (Zr cyan, O red, N blue, C gray. Hydrogen atoms are omitted for clarity)

Zr(TMPDA)$_3^{4+}$, tripositive Zr(TMPDA)$_3$(ClO$_4$)$^{3+}$ (*m/z* 284.08) complex was also observed. The ESI mass spectrum of 1:3 Zr(ClO$_4$)$_4$/TMOGA mixture in acetonitrile is shown in Figure 2 (bottom). Besides, the common species such as protonated TMOGA (HTMOGA$^+$, *m/z* 189.12) and Fe(TMOGA)Cl$^+$ (*m/z* 278.96) [21, 22], Zr(TMOGA)$_3^{4+}$ (*m/z* 163.60) was observed as a predominant species. Identification of this tetrapositive zirconium complex can be made following the Zr(TMPDA)$_3^{4+}$ case. Other peaks due to complexes with lower charges such as Zr(TMOGA)$_3$(ClO$_4$)$^{3+}$ (*m/z* 251.08) and Zr(TMOGA)$_3$(ClO$_4$)$_2^{2+}$ (*m/z* 425.80) are present in the spectrum as well with moderate abundances.

The appearance of intense peaks due to Zr(TMPDA)$_3^{4+}$ and Zr(TMOGA)$_3^{4+}$ in the mass spectra suggests that Zr^{4+} can be stabilized in the gas phase upon coordination by three TMPDA or TMOGA ligands, which retains the 4+ charge of zirconium. To get a further insight into the structures of such complexes, DFT calculations were carried out using the B3LYP functional as implemented in Gaussian09 [31–33]. Geometry optimization on the Zr(TMPDA)$_3^{4+}$ complex resulted in a C$_3$ symmetry with the metal center coordinated by six oxygen atoms and three nitrogen atoms (Figure 3), but the pyridine ring of TMPDA slightly deviates from the ligand plane. The Zr-O$_{carbonyl}$ distance was calculated to be 2.236 Å, which is close to the distances reported for other zirconium-containing

complexes [38–40] and slightly longer than that the single Zr-O bond length (2.17 Å) [41]. The Zr-N$_{pyridine}$ distance was computed to be 2.457 Å, which agrees well with those in solid-state zirconium complexes containing pyridine-based ligands (Zr-N$_{pyridine}$ distance, 2.449 Å) [42]. A similar twisted tricapped trigonal prismatic geometry was obtained for Zr(TMOGA)$_3^{4+}$, which is common for the metal-oxaglutaramides complexes [23, 24, 43–45]. The Zr-O$_{carbonyl}$ distance of Zr(TMOGA)$_3^{4+}$ was computed to be 2.215 Å, similar to that of Zr(TMPDA)$_3^{4+}$. The Zr-O$_{ether}$ distance (2.426 Å) is about the same as the Zr-N$_{pyridine}$ distance of Zr(TMPDA)$_3^{4+}$, and it is also in good agreement with the Zr-O$_{ether}$ distance (2.372 Å) in Na$_2$[Zr(oda)$_3$]·5.5H$_2$O [38]. As shown in Figure 3, both tetrapositive complexes possess nine-coordinate geometry which makes it more difficult for other neutral ligands such as H$_2$O to approach the Zr^{4+} center, thus reduces the possibility for the formation of products with lower charges during ESI.

Natural bond orbital (NBO) analysis [37] reveals that the NBO charge on zirconium is significantly reduced upon coordination by one tridentate TMPDA (2.60e) or TMOGA (2.64e) ligand (Table 1). This charge keeps decreasing with less

Table 1. NBO Charges and Sequential Binding Energies Computed at the B3LYP Level of Theory
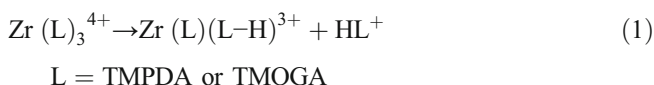
	NBO charges				ΔE (kcal/mol)
	q (Zr)	q (O$_c$)^a	q (O$_e$)^a	q (N$_p$)^a	
Zr^{4+}	4	–	–	–	–
L = TMOGA	–	− 0.59	− 0.52	–	–
Zr(TMOGA)$_1^{4+}$	2.64	− 0.75	− 0.65	–	− 848.2
Zr(TMOGA)$_2^{4+}$	2.11	− 0.72	− 0.59	–	− 334.3
Zr(TMOGA)$_3^{4+}$	1.75	− 0.68	− 0.54	–	− 124.1
L = TMPDA	–	− 0.63	–	− 0.47	–
Zr(TMPDA)$_1^{4+}$	2.60	− 0.76	–	− 0.64	− 867.6
Zr(TMPDA)$_2^{4+}$	2.07	− 0.72	–	− 0.54	− 313.1
Zr(TMPDA)$_3^{4+}$	1.63	− 0.66	–	− 0.44	− 106.9

^{a}O$_c$, O$_e$, and N$_p$ denote O$_{carbonyl}$, O$_{ether}$, and N$_{pyridine}$ respectively; ΔE is the binding energy calculated for the following reaction: Zr(L)$_{n-1}^{4+}$ + L → Zr(L)$_n^{4+}$

decrement as the number of ligand increases, consistent with the trend observed in ligated metal trications [16]. The sequential binding energies of Zr(TMOGA)$_x$$^{4+}$ (x = 1, 2, 3) were computed to be 848.2, 334.3, and 124.1 kcal/mol, indicating that coordination of the second and third ligand is much less exothermic as a result of the reduction of charge on zirconium and the increase of steric hindrance. Similar sequential binding energies were obtained for Zr(TMPDA)$_x$$^{4+}$ (x = 1, 2, 3). Note that the NBO charges on the O$_{ether}$ and N$_{pyridine}$ atoms of TMOGA and TMPDA are more negative in the ligated complexes than in the free ligand. This is due to the fact that both O$_{ether}$ and N$_{pyridine}$ atoms receive electrons transferred from other parts of the ligands such as the nitrogen atom in the N(CH$_3$)$_2$ group when they donate electrons to the metal center. Similar charge distributions were observed in the Th(TMOGA)$_x$$^{4+}$ case [23].
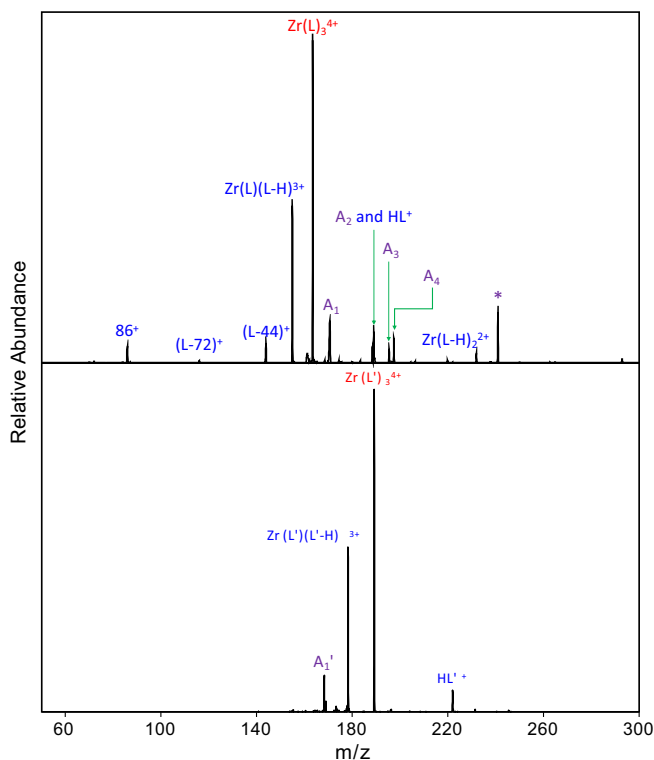
Simple tetrapositive metal complexes are rare species in the gas phase, and the chemical behaviors of these highly charged cations remain elusive. The observation of Zr(TMPDA)$_3$$^{4+}$ and Zr(TMOGA)$_3$$^{4+}$ provides an opportunity to investigate the gas-phase chemistry of tetrapositive zirconium ions supported by different neutral ligands. CID of Zr(TMOGA)$_3$$^{4+}$ (Figure 4, top) resulted in the formation of a series of multiply charged zirconium-containing species above m/z 154.96 which can be assigned following the case of Zr(TMOGA)$_3$$^{4+}$. The major fragmentation product upon CID is Zr(TMOGA)(TMOGA-

Figure 4. CID mass spectra of Zr(L)$_3$$^{4+}$and Zr(L')$_3$$^{4+}$ (L = TMOGA, top; L' = TMPDA, bottom). A$_1$, A$_2$, A$_3$, and A$_4$ are secondary products of Zr(L)(L-H)$^{3+}$, A$_1$' is a secondary product of Zr(L')(L'-H)$^{3+}$. The asterisk denotes ZrO(L)$_2$$^{2+}$ or Zr(L)(L-H)(OH)$^{2+}$. Single Zr(L)$_3$$^{4+}$ and Zr(L')$_3$$^{4+}$ isotopomers were mass selected for CID

H)$^{3+}$ (m/z 154.96) that is formed associated with HTMOGA$^+$ (Reaction 1), and other peaks between m/z 165 and 200 are secondary fragments of Zr(TMOGA)(TMOGA-H)$^{3+}$ that also appeared when Zr(TMOGA)(TMOGA-H)$^{3+}$ was mass selected as shown in Figure S1 (Supporting Information). Zr(TMOGA-H)$_2$$^{2+}$ (m/z 232.04) and ZrO(TMOGA)$_2$$^{2+}$/Zr(TMOGA)(TMOGA-H)(OH)$^{2+}$ (m/z 241.00) are the two minor CID products where the IV oxidation state of zirconium is retained. In addition, the peaks below m/z 143.92 arise from the decomposition of HTMOGA$^+$, which are commonly observed during CID of TMOGA-supported complexes [23, 24]. The CID spectrum of Zr(TMPDA)$_3$$^{4+}$ is quite simple (Figure 4, bottom), and it is dominated by the peak due to Zr(TMPDA)(TMPDA-H)$^{3+}$ (m/z 177.32, Reaction 1) and HTMPDA$^+$. The weak peak at m/z 166.96 is a secondary fragmentation product of Zr(TMPDA)(TMPDA-H)$^{3+}$ (Figure S2 in Supporting Information).

$$Zr\,(L)_3{}^{4+} \rightarrow Zr\,(L)(L-H)^{3+} + HL^+ \tag{1}$$

L = TMPDA or TMOGA

The analogous fragmentation behaviors of Zr(TMPDA)$_3$$^{4+}$ and Zr(TMOGA)$_3$$^{4+}$ suggest the fragmentation chemistry of tetrapositive zirconium complexes is not significantly affected by the ligand. Since loss of protonated ligand dominates the CID processes (Reaction 1), it is clear that tetrapositive Zr(TMPDA)$_3$$^{4+}$ and Zr(TMOGA)$_3$$^{4+}$ complexes prefer to undergo concerted reactions to form Zr^{IV}(TMPDA)(TMPDA-H)$^{3+}$ and Zr^{IV}(TMOGA)(TMOGA-H)$^{3+}$ rather than lose ligand cation to form Zr^{III}(TMPDA)$_2$$^{3+}$ and Zr^{III}(TMOGA)$_2$$^{3+}$. The oxidation state in the latter two complexes is III which is uncommon in the coordination chemistry of zirconium [1]. CID of both tetrapositive ions did not yield any detectable Zr^{4+} supported by one or two neutral ligands, and no other Zr(TMPDA)$_n$$^{4+}$ and Zr(TMOGA)$_n$$^{4+}$ (n = 1, 2, 4, or higher) complexes were observed in the ESI spectra (Figure 2) regardless of the Zr/ligand mole ratio in solution (1:0.2 to 1:5). All these experimental results indicate that three ligands are necessary and sufficient to stabilize Zr^{4+} against charge reduction in the gas phase.

The observation of Zr(TMOGA)$_3$$^{4+}$ makes it possible to compare the fragmentation behavior of another tetrapositive complex Th(TMOGA)$_3$$^{4+}$ which was recently characterized [23]. The most common oxidation state of thorium and zirconium is IV, but their CID behaviors are completely different. Th(TMOGA)$_2$(TMOGA-86)$^{3+}$ is the major fragmentation product while the yield of Th(TMOGA)(TMOGA-H)$^{3+}$ is much lower. Since other lower oxidation states for both zirconium and thorium are not easily accessible [1], the fragmentation behaviors of both tetrapositive complexes are mainly governed by the size of metal ions. As a result, it is more favorable for thorium to form the Th(TMOGA)$_2$(TMOGA-86)$^{3+}$ complex than for zirconium to form Zr(TMOGA)$_2$(TMOGA-86)$^{3+}$. The radius of Th^{4+} is large enough (0.94 Å) [10] to accommodate two TMOGA and one TMOGA-86 ligands the latter of which is presumably bound to

thorium via both ether and carbonyl oxygens. For Zr^{4+}, a Zr(TMOGA)(TMOGA-H)$^{3+}$ complex with less coordination number is formed due to its small radius of 0.72 Å [10]. The computed structure of Zr(TMOGA)(TMOGA-H)$^{3+}$ is shown in Figure S3 (Supporting Information) where the six-coordinate zirconium is essentially coordinated by three ligands: TMOGA, 86-H (dimethyl acetamide-2H) and TMOGA-86. This complex is formed via the proton loss from N(CH$_3$)$_2$ which is 27.4 kcal/mol more stable than the complex which loses a proton from CH$_2$ of TMOGA. This is also consistent with the fact that both Zr(TMPDA)$_3^{4+}$ and Zr(TMOGA)$_3^{4+}$ gave the same type of CID product with the loss of HL$^+$ although there is no CH$_2$ in the TMPDA ligand.

Conclusion

In summary, ESI of 1:3 Zr(ClO$_4$)$_4$ and TMPDA/TMOGA mixtures in acetonitrile resulted in the formation of abundant tetrapositive Zr(TMPDA)$_3^{4+}$ and Zr(TMOGA)$_3^{4+}$ complexes in the gas phase. DFT calculations at the B3LYP level of theory reveal that Zr(TMOGA)$_3^{4+}$ possesses a D$_3$ symmetry and a C$_3$ symmetry was obtained for Zr(TMPDA)$_3^{4+}$ due to the slight deviation of the pyridine ring from the ligand plane. The Zr^{4+} ion in Zr(TMPDA)$_3^{4+}$ is coordinated by six O$_{carbonyl}$ and three N$_{pyridine}$ atoms from three TMPDA ligands forming a twisted tricapped trigonal prismatic geometry. A similar nine-coordinate geometry was obtained for Zr(TMOGA)$_3^{4+}$ which also has analogous NBO charge distributions and sequential binding energies to Zr(TMPDA)$_3^{4+}$. The major CID patterns of Zr(TMPDA)$_3^{4+}$ and Zr(TMOGA)$_3^{4+}$ are very similar, and formation of charge reducing product Zr(L)(L-H)$^{3+}$ along with HL$^+$ (L = TMPDA or TMOGA) was observed in both cases. The absence of Zr(L)$_n^{4+}$ (n = 1, 2, or 4) in either ESI or CID experiments reveals that gaseous Zr^{4+} can only be stabilized by three TMPDA or TMOGA ligands so that the tetrapositive charge of the whole complex is preserved. The observation of both Zr(TMPDA)$_3^{4+}$ and Zr(TMOGA)$_3^{4+}$ complexes demonstrates that neutral TMPDA and TMOGA ligands exhibit remarkable ability to stabilize metal tetracation such as Zr^{4+} in the gas phase in spite of the very high 4th IE of zirconium (34.34 eV) which is beyond the definitive 4th IEs of actinides.

Funding Information

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