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Formation and unimolecular dissociation of $Al^{3+}(DMSO)_n$ complexes

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Abstract

Density functional theory (DFT) calculations at the B3LYP/6-31+G(d) level have been performed to follow up the formation and dissociation of $Al^{3+}(DMSO)_n$ complexes ($n = 1$–3) in the gas phase. Different exit channels are examined and transition states for unimolecular dissociation processes have been located. These channels include loss of neutral (DMSO, CH_3, and CH_4) as well as charged ($DMSO^+$, $(CH_3)_2S^+$, $CH_3{}^+$, and $DMSOH^+$) fragments. The minimum number (n_{min}) of DMSO ligands needed to stabilize Al^{3+} is 2. Loss of the neutral species is energetically unfavorable and release of DMSO needs high coordination number. On the other hand, charge-separation processes (loss of $DMSO^+$, $CH_3{}^+$, and $(CH_3)_2S^+$) are thermodynamically feasible. The loss of a methyl cation is thermodynamically the most favorable process for $n = 2$, while the loss of the dimethyl thioether cation is the preferred one for $n = 3$. Nevertheless, the presence of sizable kinetic energy barriers (40–89 kcal/mol) hinders such transformation and yields metastable $Al^{3+}(DMSO)_{2,3}$ complexes. Therefore, DMSO di- and triligated Al trications form kinetically metastable species and could be observed in the gas phase. Comparison with the available experimental data is presented and could motivate further studies.

Keywords: Ligated metal trications; Stability; Dissociation; DFT; Barrier heights

1. Introduction

The interest in the finite solvation of multicharged metal ions in the gas phase has witnessed much progress during the last decade. Although gas phase metal–ligand interactions have been studied several decades ago, most investigations have been devoted to single charged ions since the multicharged ones were not accessible until early 1990s [1–4]. The first ionization energy (IE) of most common solvents lie in the range 9–13 eV, while the second IE of metal atoms are, with few exceptions, above 12 eV. Hence, electron transfer from a neutral ligand to a multiply ionized metal atom is exothermic and occurs spontaneously on contact followed by dissociation due to Coulomb repulsion [5]. This hinders sequential ligation of metal dications in a manner similar to that which occurs with singly charged ions [1–4].

Many metals of chemical and biochemical importance occur in higher oxidation states, e.g., Zn(II), Cu(II), Mg(II), Ni(II), Fe(III), etc. but for these the study of individual ion–solvent complexes presents a number of experimental challenges. Three experimental methodologies have been used to generate ligated metal polycations, namely pick-up [6–12], electrospray ionization (ESI) [1–4,13–25], and charge stripping (CS) [26] techniques. Most experimental investigations have been devoted to studying the interaction of common solvents with a variety of metal dications [6–17,21–26]. Despite the difficulty in their generation, complexes of trications have been reported for aprotic solvents: acetonitrile [8,18,24], DMSO [1,19,24], dimethyl formamide [1], and acetone [8,24].

Two parameters have been introduced to characterize the stability of multicharged systems against dissociation [7,10,13,15–22]. These are defined as minimum (n_{min}) and critical (n_{crit}) number of ligands. The minimum number of ligands represents those ligands required to stabilize

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the cation center, whereas the critical number stands for number of ligands above which the loss of neutral ligand becomes more favorable than the dissociative electron and proton transfer. Higher values of n_{min} and n_{crit} indicate lower complex stability and propensity for reduction.

Quantum chemical calculations have also contributed to the progress of finite multicharged ion chemistry. Previously, we have investigated the existence of a variety of metal di- and trications solvated by a variety of neutral polar ligands like water [27–30], ammonia [27,28], acetone [31], acetonitrile [32], and DMSO [31,33]. These studies proved the possibility of detecting most of the studied monosolvated metal dications in the gas phase and the quantum chemical results were supported by experimental findings using CS [26] and ESI [15–17,19] techniques. It was noticed both experimentally [15–17] and theoretically [27–31] that the difficulty in generating dications of metals with a single solvent ligand tends to increase with increasing difference between the second ionization energy of metals and the first IE of a solvent. The generation of metal trications in the gas phase is expected to be more difficult because of the higher third IE of most metals (more than 19 eV) and presents experimental challenges.

The minimum size of ligated triply charged metal cations reported so far depends on both metal and ligand, where for La (third IE = 19.2 eV), one acetonitrile molecule stabilizes the La trication [18] but two [19] and five [20] molecules of DMSO and diacetone alcohol (DAA), respectively, are needed for such purpose. DMSO is among the most common aprotic solvents and its coordination with M^{2+} and M^{3+} has been studied experimentally [1–3,10,17,19,23,24] but there is still a lack of corresponding theoretical investigations [31,33]. We have recently [33] investigated the formation and dissociation of $Sc^{3+}(DMSO)_{1–6}$ and predict n_{min} of 1 and n_{crit} of 5. The latter value agrees with the reported experimental value [19] but the minimum number of ligand needed to stabilize the Sc^{3+} center was estimated experimentally to be 3. The situation for metals with higher third IE like group 13 elements (third IE for Al, for example, is 28.5 eV) is more challenging and the interaction is also complicated by a diversity of fragments generated by $M^{3+}(L)_n$ which provides a wide range of singly and doubly charged as well as neutral products. The present study is intended to provide estimation and understanding of the changes in structures and energies of different species involved in the interaction of Al^{3+}, as an example for group 13 elements, with up to three DMSO molecules. A variety of dissociation channels are expected and we will try to examine some of them in detail. In this respect we believe that quantum chemical calculations would be a very helpful tool for giving evidence for existence or absence of certain species in the gas phase. Therefore, an important feature of the present study is to predict the possibility of detecting DMSO ligated aluminum trications in the gas phase, and to complement experimental studies in this area.

2. Computations

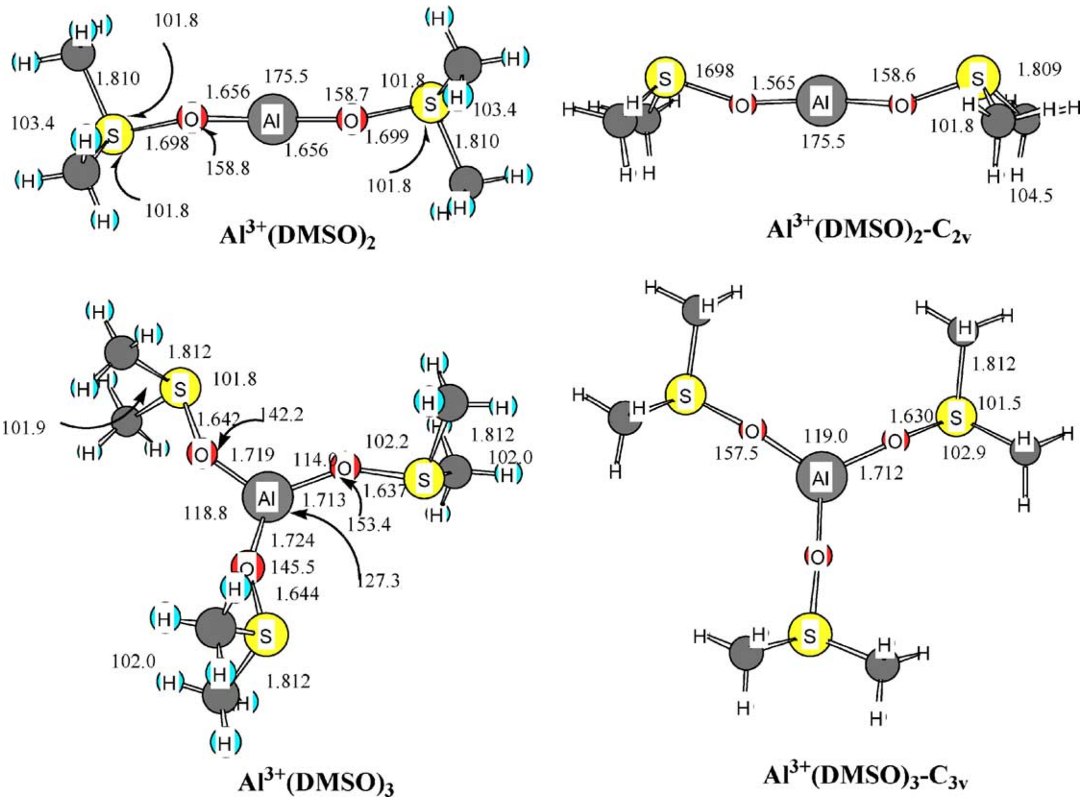
Density functional theory (DFT) calculations were carried out with the Gaussian 98W suite of programs [34]. The geometries of $Al^{3+}(DMSO)_n$, DMSO, $DMSO^+$, and different dissociation products were completely optimized at the DFT level using the B3LYP functional [35,36] and the 6-31+G(d) basis set. Search for transition states for charge-separation processes was performed with QST3 (Quasi-Newton Synchronous Transit-guided) and Eigen-Following (EF) techniques as implemented in the Gaussian 98W program [34]. Transition state location was carried out at the B3LYP/6-31+G(d) level. Acknowledging the biradical character of the transition states that correspond to the loss of $DMSO^+$ and DMS^+, we have recalculated one of them, namely the transition state for the loss of $DMSO^+$ from $Al^{3+}(DMSO)_3$, using the UBL3/6-31+G(d) method with the guess = mix option. This choice facilitates a spin-unrestricted description of systems with a multiplicity of one. The results obtained from this reassessment are identical with the previous ones. In view of this finding, the remaining transition states of biradical character were not subjected to the guess = mix analysis, since the respective computations are very time consuming.

Optimization of DMSO monoligated Al^{3+} was also performed at B3LYP and MP2(FC) methods using the 6-31+G(d) and 6-311+G(d,p) basis sets but no complex and dissociation products formed instead. The structures reported here have been characterized as local minima (zero imaginary frequency) or first-order saddle points (one imaginary frequency) on potential energy surfaces by frequency calculations at the B3LYP/6-31+G(d) level and analyzing vibrational modes. Atomic charges were calculated with the Natural Bond Orbital (NBO) program [37] implemented in G98W package using the B3LYP/6-31+G(d) densities.

The trivalent aluminum ion has a high charge (+3*e*) and small ionic radius (0.68 Å for coordination number 6) [38]. Therefore, the interaction with DMSO as a polar ligand will be mainly electrostatic and DFT at the B3LYP level was found to give reliable results in this case [27–32]. Our previous computations of multicharged systems [27–33] indicated high accuracy of B3LYP energies compared to those calculated by the CCSD(T) procedure [39]. Consequently, final energies were computed at the B3LYP/6-31+G(d) level. Our previous experience [27–33] with related systems indicated negligible contribution of Zero-point energies (ZPEs) and the features of the potential energy surfaces obtained are not affected by the ZPE corrections. The contribution of Basis Set Superposition Error (BSSE) was also insignificant [31–33]. Therefore, ZPE and BSSE corrections will not be considered here.

3. Results and discussion

The optimized structures for various species are depicted in Figs. 1 and 2. Total energies of various systems at the



$Al^{3+}(DMSO)_2$ **$Al^{3+}(DMSO)_2$-C_{2v}**

$Al^{3+}(DMSO)_3$ **$Al^{3+}(DMSO)_3$-C_{3v}**

Fig. 1. Optimized structures for $Al^{3+}(DMSO)_n$ complexes at B3LYP/6-31+G(d).

Table 1
Absolute energies (E_{abs}, a.u.) for various systems at the B3LYP/6-31+G(d) level

Species	E_{abs}	Species	E_{abs}
Al^{3+}	−240.38738	TS3–2[a]	−1347.67659
Al^{2+}	−241.45177	$Al^{2+}(DMSO)(CH_3SO)$	−1308.36000
Al^{+}	−242.14759	TS2–2[b]	−1347.70634
DMSO	−553.20012	$Al^{3+}(DMSO)(CH_3SO)$	−1307.78440
$DMSO^{+}$	−552.88072	$Al^{3+}(DMSO)(CH_2SO)$	−1307.18331
$DMSOH^{+}$	−553.54764	Al^{3+} + 3DMSO	−1899.98774
$CH_3{}^{+}$	−39.48039	$Al^{3+}(DMSO)_3$, C_1	−1901.19930
CH_3	−39.84264	$Al^{3+}(DMSO)_3$, C_{3v}	−1901.19215
CH_4	−40.52061	TS1–3[c]	−1901.05760
$(CH_3)_2S^{+}$	−477.70020	$Al^{2+}(DMSO_2)(O)$	−1423.54526
Al^{+} + DMSO	−795.34771	TS2–3[a]	−1901.06091
$Al^{+}(DMSO)$	−795.44675	$Al^{2+}(DMSO)_2(CH_3SO)$	−1861.73693
Al^{+} + 2DMSO	−1348.54770	TS3–3[b]	−1901.11402
$Al^{+}(DMSO)_2$	−1348.69728	$Al^{3+}(DMSO)_2(CH_3SO)$	−1861.22902
Al^{2+} + DMSO	−794.65189	$Al^{3+}(DMSO)_2(CH_2SO)$	−1860.62320
$Al^{2+}(DMSO)$	−794.95422	$Al^{2+}(DMSO)(CH_3SOCH_2)$	−1347.69228
Al^{2+} + 2DMSO	−1347.85190	$Al^{+}(DMSO)(O)$	−870.62858
$Al^{2+}(DMSO)_2$	−1348.33170	$Al^{3+}(DMSO)(SO)$	−1267.86080
$Al^{2+}(CH_3SOCH_2)$	−794.34048	$Al^{3+}(CH_3SO)(CH_3SO)$	−1267.88356
Al^{3+} + 2DMSO	−1346.78762	$Al^{2+}(CH_3SOCH_2)$	−1267.24627
$Al^{3+}(DMSO)_2$, C_1	−1347.76969	$Al^{3+}(DMSO)_2(SO)$	−1821.39504
$Al^{3+}(DMSO)_2$, C_{2v}	−1347.76958	$Al^{3+}(DMSO)(CH_3SO)(CH_3SO)$	−1821.41331
TS1–2[c]	−1347.67112	$Al^{2+}(DMSO)(CH_3SOCH_2)(SO)$	−1820.84824
$Al^{2+}(DMSO)(O)$	−870.12494		

[a] TS for loss of $(CH_3)_2S^{+}$ from $Al^{3+}(DMSO)_{2,3}$.

[b] TS for loss of $CH_3{}^{+}$ from $Al^{3+}(DMSO)_{2,3.}$

[c] TS for loss of $DMSO^{+}$ from $Al^{3+}(DMSO)_{2,3}$.

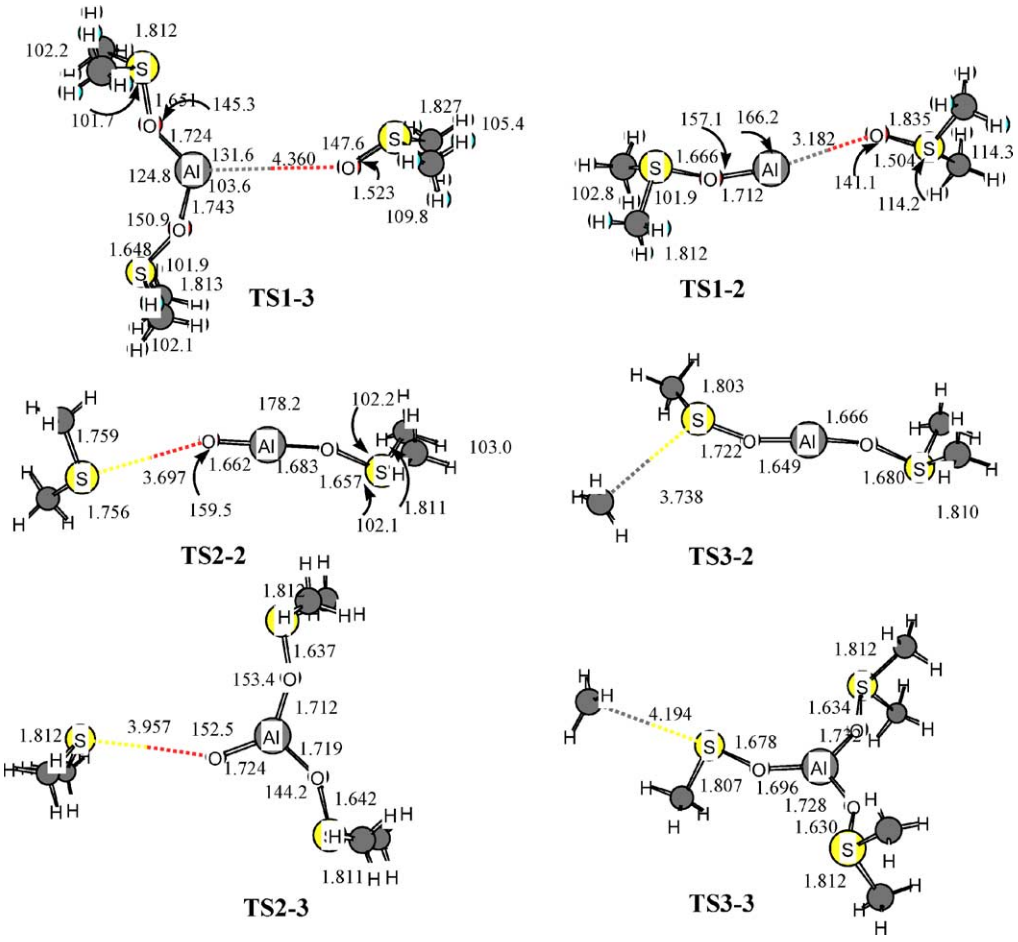


Fig. 2. Optimized structures for transition states for charge-reduction processes at B3LYP/6-31+G(d).

B3LYP/6-31+G(d) level are collected in Table 1. Relative energies of different species were computed with respect to $Al^{3+}(DMSO)_n$ complexes and are given in Figs. 3 and 4.

The IE of DMSO is lower than that of Al^{2+} by 19.4 eV. Hence, immediate charge electron transfer from DMSO to Al^{3+} is expected to occur on contact, which accounts for the absence of DMSO monoligated Al^{3+} in the gas phase [19]. All of our attempts to locate minimum structure for such species at different levels of theory failed and dissociated products are formed instead.

The binding energies of the monoligated Al^{+} and Al^{2+} ions follow the electrostatic bonding which is proportional to $Z\mu/r^2$ and, thus, the smaller the metal ion the larger the binding energy. Although the interaction between Al^{3+} ion and DMSO is expected to be strong compared to Mg^{2+}, for instance, a stable Al^{3+} complex with a single DMSO ligand could not be formed because the interaction is not strong enough to compensate for difference in IEs. Our previous computations indicated that the magnesium dication forms a thermodynamically stable complex with a single DMSO ligand that is stabilized by a kinetic barrier and expected to be observed in the gas phase [31]. On the experimental side, pick-up technique failed to detect such a Mg^{2+}DMSO complex [10]. Recently, Mg^{2+}DMSO has been generated by electrospray ionization technique and the authors reported that dications of metals with second IE > 17 eV are stabilized by two DMSO molecules [17,23]. The latter observations support our theoretical finding and give us confidence about the reliability of our data.

Geometries of the isolated ligands change upon complex formation. The dramatic effect appears in the S=O bond length and CSC and OSC angles. The S–O is elongated by 0.13–0.18 Å compared to 0.03 Å increase in the C–S bond. CSC is enlarged by ∼5° whereas CSO is contracted by ∼4°. Constraining diligated Al^{3+} complex to C_{2v} symmetry (eclipsed DMSO groups) gives a minimum structure, which is isoenergetic with another C_1 isomer where one of the methyl groups of the second DMSO is being rotated to adopt nearly a staggered configuration with respect to the first DMSO molecule, see Fig. 1. On the other hand, imposing C_{3v} symmetry on the triligated Al^{3+} complex yielded a stationary point of higher order (three imaginary frequencies). Normal mode analysis indicates that these imaginary frequencies correspond to methyl groups rotation. On relaxing the trication to adopt C_1 symmetry, its energy minimum, corresponding to optimized geometry, was found. The energy

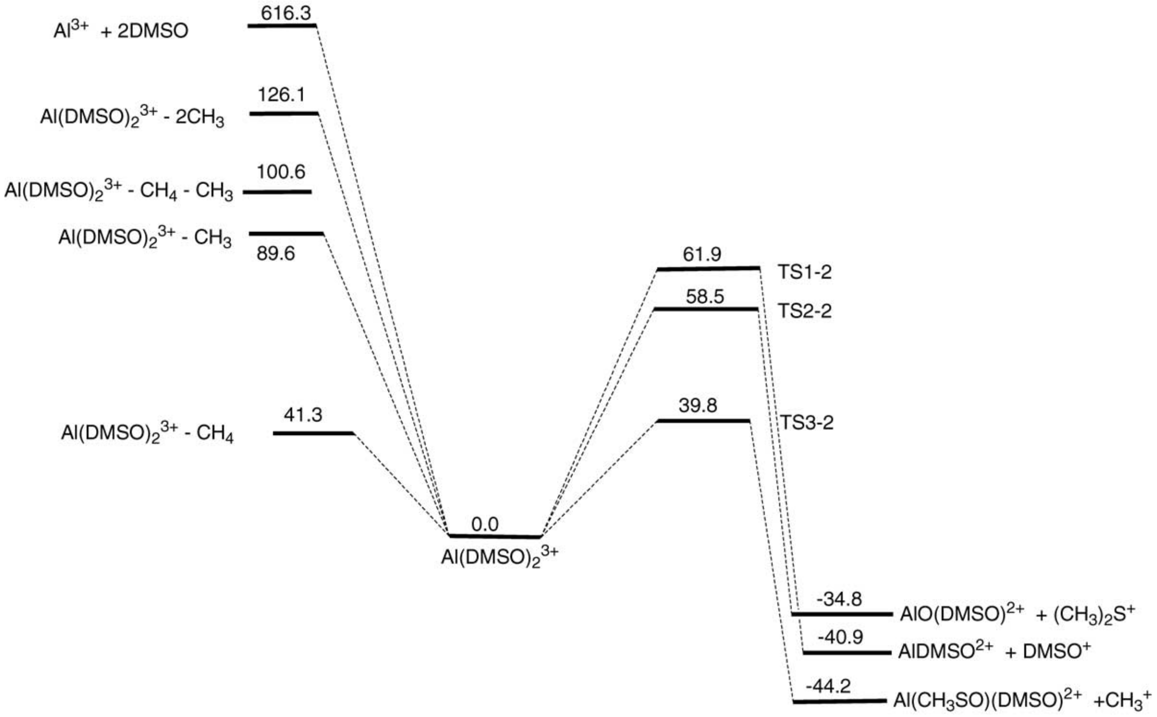


Fig. 3. Relative energies (kcal/mol) of various stationary points for $Al^{3+}(DMSO)_2$ complex at B3LYP/6-31+G(d).

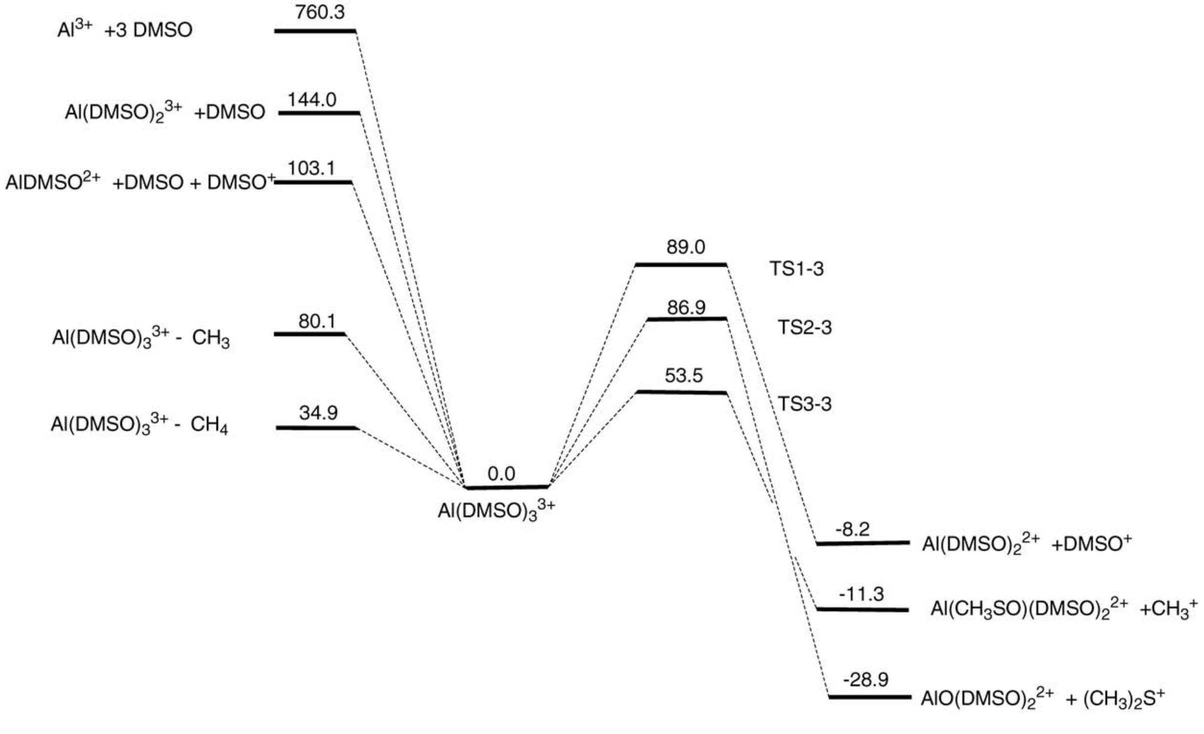


Fig. 4. Relative energies (kcal/mol) of various stationary points for $Al^{3+}(DMSO)_3$ complex at B3LYP/6-31+G(d).

difference between C_1 and C_{3v} structures is 4.5 kcal/mol in favor of the former.

For the DMSO diligated Al^{3+} complex, optimization resulted in a linear structure, and for the triligated one, in a slightly distorted trigonal form. Previously [27,29–31], we have noted that the absence of charge transfer leads to linear or planar structures so as to maximize ion dipole interaction, whereas its presence favors bent or pyramidal ones. The arrangement of two DMSO molecules around the Al center occupies a quasi-linear configuration and indicates sp hybridization at the metal center as indicated by the s and p orbital contributions to bonding as yielded by NBO analysis, namely $sp^{1.1}$. The configuration at the oxygen atoms of the DMSO ligands deviates from linearity to allow for charge transfer where 0.2e from each oxygen atom are transferred to the empty 3p orbital of the Al center. This type of interaction represents the most important effect among orbital interactions between Al^{3+} and DMSO orbitals. This interaction contributes 52 kcal/mol to the total interaction energy of 616.3 kcal/mol in the DMSO diligated Al^{3+} complex as emerging from energy analysis of the Fock-matrix in the NBO basis. Similarly, the charge transfer from water to 3d transition metal dications (Mn^{2+}–Cu^{2+}) was found to be substantial [29] but small for alkaline earth metal dications [30].

Once the $Al^{3+}(DMSO)_n$ complexes are formed a variety of exit channels can occur. Based on our previous conclusions on Mg^{2+}DMSO and $Sc^{3+}(DMSO)_n$ [31,33], the DMSO ligated Al trications can undergo charge reduction by dissociative electron transfer (1). In addition, proton transfer (2), heterolytic cleavage of C–S and S–O bonds (3–6), and loss of neutral ligand (7) represent another possible channels.

$$Al^{3+}(DMSO)_n \rightarrow Al^{2+}(DMSO)_{n-1} + DMSO^+ \quad (1)$$

$$Al^{3+}(DMSO)_n \rightarrow Al^{2+}(DMSO)_{n-1} + DMSOH^+ \quad (2)$$

$$Al^{3+}(DMSO)_n \rightarrow Al^{2+}(DMSO)_{n-1}\text{–}OSCH_3 + CH_3{}^+ \quad (3)$$

$$Al^{3+}(DMSO)_n \rightarrow Al^{3+}(DMSO)_{n-1}\text{–}OSCH_3 + CH_3 \quad (4)$$

$$Al^{3+}(DMSO)_n \rightarrow Al^{3+}(DMSO)_{n-1}\text{–}OSCH_2 + CH_4 \quad (5)$$

$$Al^{3+}(DMSO)_n \rightarrow Al^{2+}(DMSO)_{n-1}\text{–}O + CH_3SCH_3{}^+ \quad (6)$$

$$Al^{3+}(DMSO)_n \rightarrow Al^{3+}(DMSO)_{n-1} + DMSO \quad (7)$$

Channels 1, 2, 3, and 6 represent charge-separation processes while other paths represents release of neutral fragments from the corresponding complex.

Loss of neutral DMSO, CH_3, and CH_4 fragments are endothermic processes with the former being the most unlikely one to occur, as can be seen from Figs. 3 and 4. With increasing number of ligands the release of neural fragments (CH_4, CH_3, and DMSO) becomes more feasible as indicated by the decrease of endothermicity with ligand number. Experimentally [19], no CH_3 loss has been observed for $n = 3$ which agrees with our prediction. The formation of methane is energetically more favorable than that of a methyl radical and the release of the first methane molecule facilitates the production of the first methyl radical. Although loss of the methyl radical is thermodynamically less favorable, its formation may be kinetically more easier than the release of a methane molecule because the latter will be formed through two steps: first is the release of a methyl radical followed by the release of a hydrogen atom from neighboring methyl groups. This procedures may be kinetically hindered and is unlikely to occur unless at high temperature.

Previously [33], we have calculated energies for dissociation of $Sc^{3+}(DMSO)_n$ for $n = 1$–6. Fig. 5 displays the correlation between energetics of unimolecular dissociation reactions of both $Al^{3+}(DMSO)_{2,3}$ and $Sc^{3+}(DMSO)_{2,3}$ complexes. The correlation is found to be impressive ($R^2 = 0.899$) and can be used to estimate the energies of unimolecular dissociation of Al^{3+} $(DMSO)_n$ for $n > 3$. From this relation we can easily determine the reaction energy of any desirable channels for Al^{3+} complexes. The loss of more neutral fragments can be deduced from Fig. 5. The loss of either methane or methyl radical is preferable over the loss of neutral DMSO molecule as noticed previously for $Sc^{3+}(DMSO)_n$ complexes [33].

The interaction between Al^{3+} and two and three DMSO molecules is strong and gives higher binding energies but the dissociation to positively charged species is thermodynamically favored. The exothermicity of these reactions decreases with increasing number of ligands. We have investigated the loss of monopositive DMSO, methyl, and dimethyl thioether for di- and triligated Al^{3+} complexes. Loss of a methyl cation is more exothermic than loss of $DMSO^+$ by 3 kcal/mol for $n = 2$, 3. On the experimental side no $DMSO^+$ has been detected whereas heterolytic cleavage of a monopositive methyl cation was observed [19]. However, the formation of charged species seems to be more feasible exit channels if there is no sufficiently high kinetic energy barrier to hinder such transformation. The transition

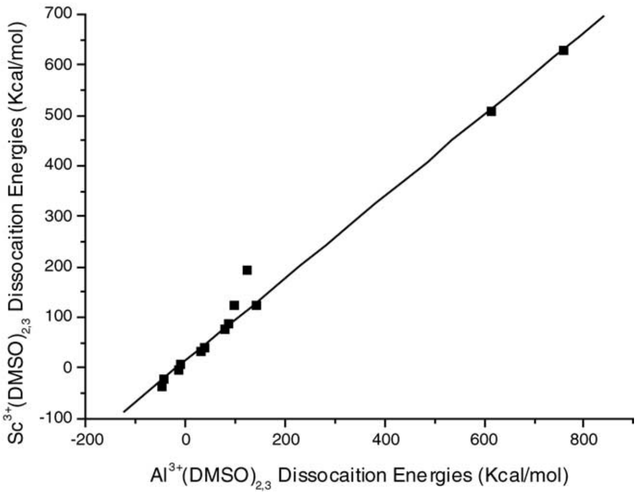


Fig. 5. Correlation between reaction energies for $Al^{3+}(DMSO)_{2,3}$ and $Sc^{3+}(DMSO)_{2,3}$ complexes.

states for charge-separation ($Al^{2+}(DMSO)_{n-1}$ + $DMSO^+$ and $Al^{2+}(DMSO)_{n-1}$–$OSCH_3$ + CH_3^+, $Al^{2+}(DMSO)_{n-1}$ + $(CH_3)_2S^+$) processes have been located at the B3LYP/6-31+G(d) level of theory and verified by the presence of only one negative imaginary frequency in the Hessian matrix. Normal mode analysis of the negative frequencies indicates that they correspond to the cleavage of the considered bonds, namely Al–O, S–O, and S–C bonds, respectively. The structures of these transition states have been analyzed with respect to electronic distribution to ensure, at least tentatively, that these TSs correspond to removal of charged and not to neutral fragments because we imposed three positive charges on the whole systems and we cannot decide whether these structures correspond to loss of neutral or charged species without examining the charge distribution.

From both theory [27–33] and experiment [15–26] thermodynamically unstable ligated metal polycations are metastable species based on the existence of Coulomb barriers and on their lifetimes. For the investigated systems, considerable Coulomb barriers (40–89 kcal/mol) have been found, which kinetically stabilize the di- and triligated Al trication in the gas phase, see Figs. 3 and 4. The highest barriers were recorded for the loss of $DMSO^+$ and the least ones for the loss of CH_3^+. Therefore, the loss of a methyl cation is favored over the loss of $DMSO^+$ from thermodynamic and kinetic point of view, which agrees with experimental finding [19]. On the other hand, loss of $DMSOH^+$ is more exothermic by 74.3 and 25.5 kcal/mol for two and three ligand systems, respectively, but this process should be accomplished in two steps, namely the release of a proton, which attaches to one of the coordinated DMSO ligands and subsequent removal of $DMSOH^+$. These two processes should involve intermediate and high-energy barriers, implying the emergence of the protonated DMSO molecule with high energy. Therefore, of the investigated DMSO ligated aluminum trications only $Al^{3+}(DMSO)_{2,3}$ would be observed because they form thermodynamically metastable trication complexes and are expected to be long-lived, based on the kinetic energy barrier, and therefore, detectible by experiment. As a matter of fact, a variety of dissociation products are formed and their abundance can be related to the height of the barrier that prevents them from being formed spontaneously. Therefore, the release of CH_3^+ is more likely than that of $DMSO^+$.

The estimated barrier heights for different exit channels increases with increasing number of ligands, which is indicative of decreasing probability for detecting charged fragments of larger complexes. Therefore, an increase in the number of ligands will enhance the production of neutral fragments and decrease the percentage of charged fragments. By using Fig. 5, we can deduce n_{crit} for $Al^{3+}(DMSO)_n$ by comparing their energies with $Sc^{3+}(DMSO)_n$. We could derive n_{crit} of 5, which agrees with the experimental findings [19].

The disagreement between computational results and experiment should motivate more studies in this field. An absence of experimental observation is not sufficient evidence for the actual non-existence of the respective species. For instance, the smallest reported hydrated copper dications were $Cu^{2+}(OH_2)_n$, $n = 15$ [3]. The value of n has been refined to 3 [11] and finally to 1 [15,26] as predicted by theory [27–29].

4. Conclusions

Interaction of Al^{3+} with DMSO ligand up to three molecules has been studied using DFT at B3LYP level with double-zeta basis sets. The results obtained can be summarized as follows:

1. Due to the large difference between IE of DMSO and second IE of Al, Al^{3+} does not form a monoligated complex with DMSO. However, the di- and triligation yield metastable complexes with the aluminum trication.
2. Thermodynamically unstable complexes are stabilized by the presence of Coulomb barriers for unimolecular dissociation.
3. Loss of charged fragments ($DMSO^+$, CH_3^+, $(CH_3)_2S^+$, and $DMSOH^+$) is energetically favorable but prohibited by the presence of sizable energy barriers. On the other hand, loss of neutral methyl radical, methane, and DMSO are energy demanding processes and unlikely occur under normal experimental conditions.
4. The loss of a methyl cation is thermodynamically the most favorable process for $n = 2$, while the loss of the dimethyl thioether cation is the preferred one for $n = 3$. Nevertheless, the presence of sizable kinetic energy barriers (40–89 kcal/mol) hinders such transformation and yields metastable $Al^{3+}(DMSO)_{2,3}$ complexes. The barrier heights for the loss of a methyl cation are the smallest among other barriers. This indicates that the loss of CH_3^+ represents the favored exit channel for $n = 2, 3$.
5. A considerable agreement with experimental data has been noticed for some of the investigated complexes. New experiments under refined experimental conditions and additional detailed theoretical investigations of all possible exit channels may be able to solve the disagreement.
6. With increasing number of ligands both the exothermicity of the charge-reduction processes and the endothermicity of the formation of neutral fragments decreases.
7. For all of the di- and tripositive metal ions investigated so far only Al^{3+} failed to form a stable monoligated compound with DMSO. To generalize our conclusions, further investigations for a larger number of ligands appear desirable.

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