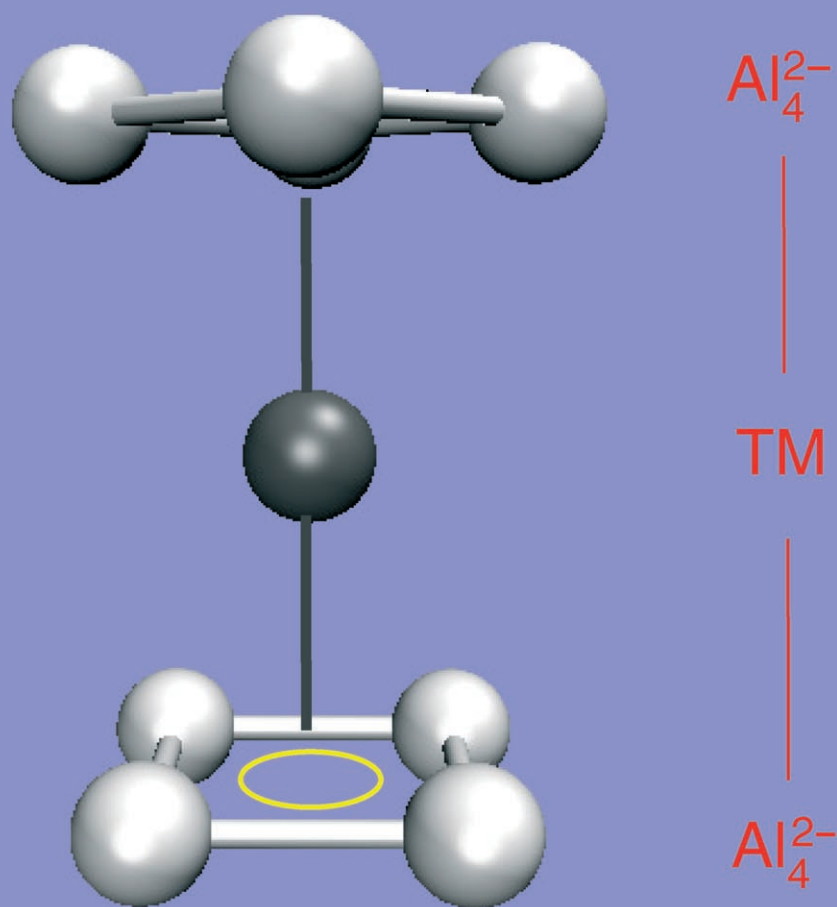


All-Metal Sandwich Complexes



For more information see the following pages

Sandwich Complexes Based on the “All-Metal” Al_4^{2-} Aromatic Ring

Jose M. Mercero,^{*[a]} Elena Formoso,^[a] Jon M. Matxain,^[b] Leif A. Eriksson,^[b] and Jesus M. Ugalde^{*[a]}

Abstract: We report on novel sandwichlike structures $[\text{Al}_4\text{MAl}_4]^{q-}$ ($q=0-2$ and $\text{M}=\text{Ti}, \text{V}, \text{Cr}, \text{Zr}, \text{Nb}, \text{Mo}, \text{Hf}, \text{Ta}$ and W) based on the recently synthesized all-metal aromatic Al_4^{2-} square ring. The sandwichlike structures have two aromatic tetraaluminum square rings which trap a transition-metal cation from either the first, second, or

third row. The stability of the anionic sandwichlike complexes towards electron detachment is discussed, and addi-

Keywords: aluminum · aromaticity · density functional calculations · sandwich complexes · transition metals

tion of alkali cations is found to stabilize the $2-$ charged complexes, preventing spontaneous electron detachment. Once the sandwichlike complexes are formed, the Al_4^{2-} square properties remain nearly unchanged; this fact strongly supports the hypothesis that in these complexes the Al_4^{2-} square rings remain aromatic.

Introduction

The recently synthesized Al_4^{2-} aromatic square ring countered by alkali cations^[1] has gained much attention,^[2] since this aromatic all-metal square ring has properties that are usually associated with organic molecules. The unexpected large resonance energy of Al_4^{2-} has been attributed to the multiple-fold aromaticity,^[3,4] a concept first introduced by Schleyer^[5] and later experimentally confirmed by Berndt.^[6,7] Multiple-fold aromaticity applies to molecules that possess more than one independent delocalized bonding system, either σ or π type, each of them satisfying the $4n+2$ electron Hückel counting rule of aromaticity. This concept helps the understanding of *simultaneous* contributions to aromaticity within the same molecular structure as arising from various delocalized bonding systems, and should be of general ap-

plicability irrespective of whether the molecule is organic or inorganic.^[8]

Following the characterization of the Al_4^{2-} molecule, analogous structures formed by Ga_4^{2-} , In_4^{2-} ^[9] and XAl_3^{2-} ($\text{X}=\text{Si}, \text{Sn}, \text{Ge}$ and Pb)^[10] have also been synthesized. The metal rings of these compounds present properties similar to Al_4^{2-} , namely, high magnetic shielding,^[11] large ring current,^[12] similarly derived antiaromatic structures^[13] and large resonance energies.^[3,14]

The chemistry of these exciting novel all-metal aromatic rings is now starting to develop. In particular, one interesting feature is the possibility that Al_4^{2-} could be incorporated into sandwich complexes.^[15] We recently reported the computational prediction of the first transition-metal complex, that is, the $[\text{Al}_4\text{TiAl}_4]^{2-}$ sandwich complex,^[16] based on the all-metal Al_4^{2-} aromatic ring. Although this dianionic compound is not stable towards spontaneous electron detachment, the $\text{Na}[\text{Al}_4\text{TiAl}_4]^-$ species is stable^[16] and provides an opportunity for experimental studies of this novel sandwich complex. Furthermore, in an interesting recent paper, Datta and Pati^[17] have proposed various examples of stable transition-metal complexes of the all-metal π -antiaromatic and σ -aromatic Al_4^{4-} moiety.

In the present manuscript, we report that all the early transition metals of the first, second, and third rows can also form stable sandwich complexes with the Al_4^{2-} ring. The sandwich complexes presented herein are isoelectronic, with a net charge of $2-$, $1-$, and 0 for the elements of the Ti, V, and Cr groups in the periodic table, respectively. In the following we first discuss various salient properties of these

[a] Dr. J. M. Mercero, E. Formoso, Prof. J. M. Ugalde
Kimika Fakultatea, Euskal Herriko Unibertsitatea, and
Donostia International Physics Center (DIPC)
P.K. 1072 20080 Donostia, Euskadi (Spain)
Fax: (+34) 943-015270
E-mail: jm.mercero@ehu.es

[b] Dr. J. M. Matxain, Prof. L. A. Eriksson
Department of Natural Sciences and Örebro Life Science
Center, Örebro University, 70182 Örebro (Sweden)
Fax: (+34) 943-015270

Supporting information for this article is available on the WWW under <http://www.chemistry.org> or from the author. It contains cartesian coordinates, molecular orbitals and harmonic vibrational spectra of the sandwich-like complexes $[\text{Al}_4\text{MAl}_4]^{q-}$, with $q=2, 1, 0$ and $\text{M}=\text{Ti}, \text{V}, \text{Cr}, \text{Zr}, \text{Nb}, \text{Ta}, \text{Mo}, \text{Hf}, \text{Ta}, \text{W}$.

novel structures, such as the aromaticity changes of the aluminum square rings upon interaction with the transition metal and the electron detachment energies (EDE), a property used experimentally to detect similar structures.^[1,15] Finally, we have added appropriate counterions (alkali metal cations) to the 2- charged sandwiches (Ti, Zr, and Hf) in order to protect them from spontaneous electron detachment and, hence, obtain stable structures amenable to experimental detection.

Computational Methods

The B3LYP functional, as implemented in Gaussian 03,^[18] with the standard 6-311+G* basis set (for aluminum and first-row transition metals) was employed for the geometry optimizations and normal mode vibrational analyses, given the earlier satisfactory validation of the method for these kinds of molecules.^[19] For Zr, Nb, Mo, Hf, Ta, and W the energy adjusted Stuttgart effective core potentials (ECP) were used.^[20] All the optimizations were started from appropriately biased sandwich structural motifs and were confirmed to be real minima on the corresponding potential energy surface (PES). Nevertheless, it is worth noting that they might not be the absolute minima. Structures with the transition metal segregated from a hollow Al₈ cluster might be considered as serious contenders for the structural motif of the absolute minimum energy isomer.^[21] However, in view of the substantial structural rearrangement required to transit between these two types of structural motifs, we anticipate that sandwich complexes could be seen as stable enough structures. Despite its widespread use, aromaticity is more a concept rather than a directly measurable quantity. Consequently, measurements of aromaticity rely on many diverse criteria.^[22] Among them, the nucleus-independent chemical shift (NICS), based on the "absolute magnetic shielding" taken at the center of a ring compound, is widely used and has been proven to be accurate for ordinary cyclic carbon compounds.^[23] Recently the method has also been successfully used for inorganic cyclic aromatic compounds,^[23–25] including the characterization of the so-called d-orbital aromaticity.^[8,26–28] Thus, the NICS values were calculated also at the B3LYP/6-311+G* level of theory. A positive value of the NICS indicates that the molecule is antiaromatic, a negative value indicates the aromaticity of the molecule. The NICS calculated at the center of the square (NICS(0)) describes the σ aromaticity and the NICS out of the square plane (NICS(1)) describes the π aromaticity of the molecule.

The electron detachment energies (EDE) were calculated following various approaches. Thus, the vertical EDE was calculated as the difference between the $-n$ charged structure energy and the $-n+1$ charged structure, with the geometry of the $-n$ charged structure. The photoelectronic spectra, given by the unrestricted outer valence Green function (UOVGF) methodology (as implemented in Gaussian 03), were also calculated with the 6-311+G* basis set. The large values of the pole strengths obtained in the UOVGF calculations suggest that the electron dissociation channels are one-electron processes.

The MOLDEN program^[29] was used to draw the structures and orbitals.

Results and Discussion

Geometries and aromaticity: All the sandwich structures characterized in the present work have D_{4d} symmetry (see Figure 1). Some of the sandwiches required symmetry relaxation to remove a few small negative force constants. In all cases the structural relaxation was very small.^[30] Despite of the small distortion away from the D_{4d} symmetry, the orbitals have been labeled in accordance with the irreducible

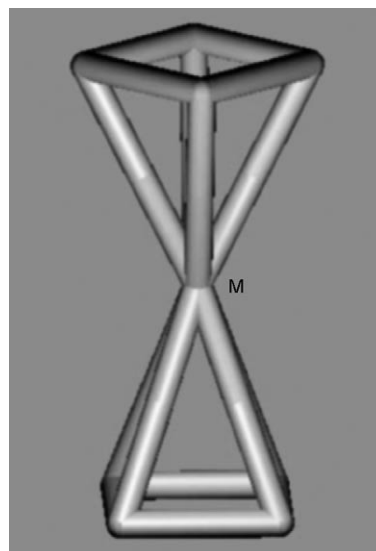


Figure 1. Staggered $[Al_4MAl_4]^{q-}$ ground state structure (D_{4d} symmetry) for $M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta$ and W , with charges $q=2$, for Ti, Zr and Hf , $q=1$ for V, Nb and Ta , and $q=0$ for Cr, Mo and W , respectively.

representations of the D_{4d} crystallographic group in all the complexes.

The deformation of the two Al_4^{2-} rings is negligible after the sandwich complex is formed with the transition metal in the middle. The Al–Al bond length in the Al_4^{2-} square is 2.591 Å, and increases 2.74–2.84 Å upon complex formation.

The Al–Al bond length increases slightly as we move to the right and down in the periodic table. Thus, W is the transition metal that yields the largest Al–Al elongation, from 2.591 Å in the plain Al_4^{2-} square ring to 2.837 Å in the W sandwich complex.

The main geometric difference of the sandwich complexes appears in the distance between the transition metal and the center of the aluminum rings, which shrinks when going to the right in the periodic table. Recall that as we move to the right in the periodic table the total charge of the complexes decreases from 2- for the Ti group of complexes to 0 for the Cr group of complexes (see Table 1). The reduced distance from the transition metal to the center of aluminum ring can easily be viewed as an effect due to the distribution of the total charge within the system. We can think of these complexes as being built by two tetraaluminum square rings with a nominal charge of 2-, and transition-metal cations with formal charges of 2+ (Ti), 3+ (V), and 4+ (Cr) (analogously for the second- and third-row transition metals). Due to the Coulombic attraction between the charged moieties the distance between the transition metal and the Al_4^{2-} rings should decrease. On the contrary, the distance increases slightly as we move down the periodic table as a consequence of the moderate increase in size of the transition metals.

One of the most remarkable properties of the Al_4^{2-} ring is its double aromaticity,^[3,12,31] as revealed by the negative

Table 1. Selected properties of the molecules calculated at the B3LYP/6-311+G* level of theory. The bond lengths are given in Å and the NICS values in ppm.

| | [Al ₄ TiAl ₄] ²⁻ (D _{4d}) | [Al ₄ VAl ₄] ⁻ (D _{4d}) | [Al ₄ CrAl ₄] ⁰ (D _{4d}) | Al ₄ ²⁻ |
|----------------------------------|--|--|--|-------------------------------|
| R _{Al-Al} | 2.744 | 2.747 | 2.760 | 2.591 |
| R _{C-TM} ^[a] | 1.882 | 1.715 | 1.626 | |
| R _{Al-C} | 1.940 | 1.943 | 1.952 | 1.833 |
| NICS(0) | -36.86 | -49.82 | -37.08 | -34.45 |
| NICS(1) | -16.80 | -17.03 | -8.59 | -27.38 |
| | [Al ₄ ZrAl ₄] ²⁻ (D _{4d}) | [Al ₄ NbAl ₄] ⁻ (C ₁ ^[b]) | [Al ₄ MoAl ₄] ⁰ (C ₁ ^[b]) | |
| R _{Al-Al} | 2.754 | 2.786 | 2.818 | |
| R _{C-TM} | 2.060 | 1.850 | 1.724 | |
| R _{Al-C} | 1.948 | 1.970 | 1.993 | |
| NICS(0) | -31.12 | -27.41 | -17.58 | |
| NICS(1) | -18.54 | -17.52 | -14.92 | |
| | [Al ₄ HfAl ₄] ²⁻ (D _{4d}) | [Al ₄ TaAl ₄] ⁻ (C ₁ ^[b]) | [Al ₄ WAl ₄] ⁰ (C ₁ ^[b]) | |
| R _{Al-Al} | 2.763 | 2.800 | 2.837 | |
| R _{C-TM} | 2.062 | 1.856 | 1.731 | |
| R _{Al-C} | 1.954 | 1.980 | 2.006 | |
| NICS(0) | -25.49 | -21.06 | -13.26 | |
| NICS(1) | -15.99 | -14.56 | -12.16 | |

[a] C denotes the center-of-mass of the Al₄ rings. [b] The distortion of these sandwiches with respect to the D_{4d} symmetry is minute, but necessary to remove some small imaginary vibrational modes.

values of both NICS(0) and NICS(1), shown in Table 1. Once the ring interacts with the transition metal to form the sandwich complex, both aluminum rings maintain their two-fold aromaticity (see NICS(0) and NICS(1) values in Table 1). Comparing the NICS(0) values of the tetraaluminum rings before and after complexation, we note that the σ aromaticity is enhanced upon complexation only for the first-row transition metals, while both NICS values for the rest of the complexes decreases. We also observe that the σ aromaticity decreases as the transition metals move right and down the periodic table, except for Ti. Thus, the largest observed σ aromaticity of the Al₄ rings is seen for the V sandwich complex, while the W sandwich complex has the smallest NICS(0) value. The π aromaticity also decreases when the transition metal moves right (again Ti is the exception) but not down, the second-row transition-metal sandwich complexes being those for which the π aromaticity of the aluminum rings is the largest.

In summary, for the first-row transition metal sandwich complexes, the tetraaluminum square rings have larger σ aromaticity than the plain Al₄²⁻ square ring. In contrast, the π aromaticity of these rings is the lowest. For the second- and third-row transition-metal sandwich complexes, the aluminum rings have lower NICS(0) and NICS(1) values, indicating that both the σ and π aromaticities decrease upon complex formation.

The analysis of the molecular orbitals sheds additional light on the aromaticity of these sandwich complexes.^[2] Recall that, π-aromatic molecules are those that have full occupation of the delocalized bonding π orbitals and analogously for σ aromaticity. Antiaromaticity, in contrast, is associated with either incomplete occupation of the delocalized

π/σ bonding orbitals or to partial occupation of the delocalized π/σ antibonding orbitals. Al₄²⁻ constitutes a rare example of multiple-fold aromaticity,^[1,9] possessing one π-aromatic system with two electrons and two σ-aromatic systems with two electrons each. Note that all the three systems fulfil the Hückel (4n+2) electron counting rule with n=0.

We have analyzed the molecular orbitals of all nine sandwich complexes, but for the sake of clarity only the molecular orbitals of Al₄CrAl₄ are depicted in Figure 2. The orbi-

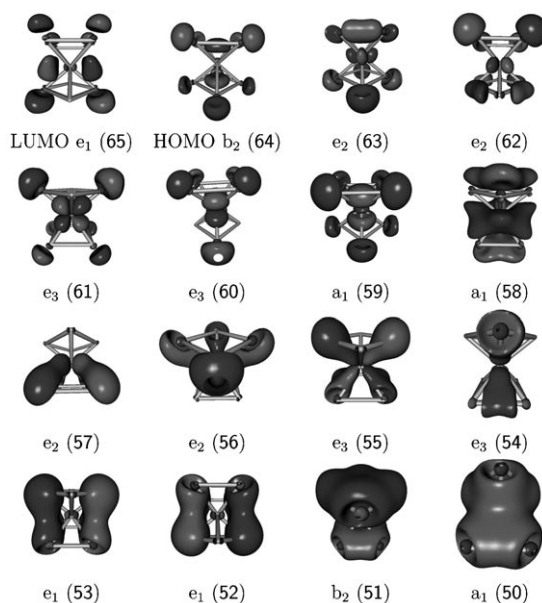


Figure 2. Valence molecular orbitals of the Al₄CrAl₄ sandwich complex. The orbital number is shown in parentheses.

tals of the nine sandwich complexes are very similar (available as Supporting Information). From the inspection of Figure 2, the three aromatic systems of each of the two Al₄²⁻ moieties are clearly observed. Thus, the HOMO and the molecular orbital 59 correspond to the two σ tangential systems of the two tetraaluminum rings, molecular orbitals 62 and 63 to the two σ radial systems, and molecular orbitals 51 and 58 constitute the occupied molecular orbitals of the π system. This, along with the small changes in the two Al₄²⁻ geometries upon complexation with the transition metals, is very supportive of the strong structural integrity of the tetraaluminum ring and reinforces the hypothesis that the Al₄²⁻ unit could be incorporated as a building block into different inorganic materials.

Electron detachment energies: The analogy between these sandwich complexes and metallocenes, in the sense that a transition metal donates electrons into two rings stabilizing them due to resonance, suggests that these sandwich complexes should be stable. The anionic character of the Ti, V, Zr, Nb, Hf, and Ta sandwich complexes, however, may destabilize their structures towards spontaneous electron de-

Table 2. Electron detachment energies obtained using the vertical (VDE), and unrestricted outer valence green functions (VGF) methods. Units are eV. Sym stands for the orbital symmetry from which the electron dissociates.

| Complex | s | VDE | Sym | VGF | Pole strength | Sym | VGF | Pole strength | Sym | VGF | Pole strength |
|--|-----------------|--------|-----------------|--------|---------------|-----------------|--------|---------------|-----------------|--------|---------------|
| [Al ₄ TiAl ₄] ²⁻ [a] | b ₂ | -1.051 | b ₂ | -0.789 | 0.931 | e ₂ | -0.543 | 0.935 | a ₁ | -0.031 | 0.843 |
| [Al ₄ VAl ₄] ⁻ | b ₂ | 2.494 | b ₂ | 2.316 | 0.917 | e ₂ | 2.947 | 0.889 | a ₁ | 3.267 | 0.866 |
| [Al ₄ CrAl ₄] ⁰ | b ₂ | 5.583 | b ₂ | 5.749 | 0.898 | e ₂ | 6.249 | 0.876 | a ₁ | 6.932 | 0.859 |
| [Al ₄ ZrAl ₄] ²⁻ | e ₃ | -0.803 | e ₃ | -1.130 | 0.920 | b ₂ | -0.389 | 0.865 | e ₂ | -0.099 | 0.945 |
| [Al ₄ NbAl ₄] ⁻ | b ₂ | 2.431 | b ₂ | 2.503 | 0.890 | e ₂ | 3.020 | 0.915 | a ₁ | 3.576 | 0.845 |
| [Al ₄ MoAl ₄] ⁰ | b ₂ | 5.708 | b ₂ | 6.017 | 0.908 | e ₂ | 6.783 | 0.923 | a ₁ | 7.261 | 0.863 |
| [Al ₄ HfAl ₄] ²⁻ | e ₃ | -0.850 | e ₃ | -1.153 | 0.902 | b ₂ | -0.334 | 0.855 | e ₂ | -0.117 | 0.958 |
| [Al ₄ TaAl ₄] ⁻ | b ₂ | 2.473 | b ₂ | 2.590 | 0.881 | e ₃ | 2.536 | 0.890 | e ₂ | 3.070 | 0.908 |
| [Al ₄ WAl ₄] ⁰ | b ₂ | 5.743 | b ₂ | 6.077 | 0.896 | e ₂ | 6.802 | 0.897 | - | - | - |
| Al ₄ ²⁻ [a] | a _{1g} | -1.670 | a _{1g} | -1.714 | 0.861 | a _{2u} | -1.686 | 0.847 | b _{2g} | -1.650 | 0.851 |

[a] Discrepancies between the VGF at the present manuscript and the data published in reference [16] arise mainly from the VGF calculation using GAUSSIAN 03 in the former and GAUSSIAN 98 in the latter.

tachment. It must be recalled, that Al₄²⁻ itself has not been detected on its own, but countered by various alkali (Li, Na), or transition metals (Cu).^[1] The Al₄²⁻ aromatic square ring is unstable towards electron detachment due to the Coulomb repulsion. This instability has been estimated to be -1.714 eV (see Table 2). The negative value indicates that the molecule is more stable as a mono- rather than as a dianion. Consequently, counterions are customarily added to protect the anions from electron detachment.^[2]

The vertical and UOVGF EDE's of the anionic structures are reported in Table 2. Inspection of Table 2 reveals that as soon as the total charge is reduced from 2- to 1-, the EDE's become positive. This indicates that the V, Nb, Ta, Cr, Mo, and W sandwich complexes are stable towards electron detachment. The values provided by the vertical EDE and UOVGF approaches agree satisfactorily. For the 2- charged sandwich complexes both approaches predict that an electron detaches spontaneously.

For the Ti complex the electron detaches from the b₂ orbital, whereas for the Zr and Hf complexes the electron detaches from one of the doubly degenerate e₃ orbitals. These two compounds are the only ones for which the electron detaches from an e₃ orbital. For the rest of the sandwiches this orbital corresponds to the highest b₂ orbital (these orbitals are analogous to the higher occupied molecular orbitals having the same symmetry shown in Figure 2, and available as Supporting Information). The EDE for the Ti sandwich complex is smaller than that of Zr and Hf (0.79 vs. 1.1 eV), while for the rest of the complexes that have the same charge the EDE values are similar, that is, the UOVGF's for V, Nb and Ta are 2.32, 2.50 and 2.59 eV, respectively.

Stabilization of the [Al₄MAl₄]²⁻ complexes: As mentioned above, the [Al₄MAl₄]²⁻ (M = Ti, Zr and Hf) complexes have negative electron detachment energies indicating that the monoanions are more stable than the dianions and hence spontaneous electron detachment can take place, assuming the barriers to be small, as was found for the Al₄²⁻ square ring.^[2] Experimentalists have added counterions in order to reduce the total charge, and render an stable molecule amenable to experimental detection. Thus, Li et al.^[1] have been

able to detect the Al₄²⁻ square ring countered by different alkali, and fully characterized their structures by using the photoelectron spectroscopy and ab initio calculations. The same procedure could be followed for the [Al₄{Ti/Zr/Hf}Al₄]²⁻ structures described herein. In a previous study,^[16] we reported the structures formed by [Al₄TiAl₄]²⁻ with one and two Na⁺ cations. We present here the structures formed by the three complexes [Al₄MAl₄]²⁻ (M = Ti, Zr, and Hf) with the small alkali ions, Li⁺, Na⁺, and K⁺.

The obtained complexes between the alkali cations and [Al₄MAl₄]²⁻ are similar to the previously reported Na-[Al₄TiAl₄]⁻ complex.^[16] Namely, the cation interacts with one of the aluminum rings rather than with the transition metal. All attempts to locate structures in which the alkali cation interacts with the transition metal were unsuccessful. It is worth noting that for the closely related Li[N₄TiN₄]⁻ sandwich complex,^[32] a structure with Li⁺ interacting with the titanium was found. The geometrical and NICS data obtained for the {Li/Na/K}[Al₄{Ti/Zr/Hf}Al₄]⁻ complexes are shown in Table 3 and Figure 3.

The mode of interaction of the alkali cations with [Al₄{Ti/Zr/Hf}Al₄]²⁻ sandwich complexes (see Figure 3) is reminiscent of their interaction with the bare Al₄²⁻ ring.^[1] Thus, we found that the alkali cation interacts with one edge of an aluminum ring, causing a minor distortion to its perfect square geometry. The alkali cations lie on top of one of the Al₄ ring edges at an angle (α in Table 3 and Figure 3) around 110–130° with respect to the tetraaluminum ring plane. The angles are around 130° for all alkali cations in the Ti complexes. This angle is slightly smaller in the Zr and Hf complexes, and is reduced as the size of the alkali cation increases. The reduction is especially large for the K-[Al₄HfAl₄]⁻ complex in which the angle is only 71.3°.

Comparing the tetraaluminum rings of the alkali sandwich complexes with those of the plain [Al₄{Ti/Zr/Hf}Al₄]²⁻ sandwich complexes, tiny distortions can be observed as a consequence of the interaction with the alkali cation. Thus, the aluminum ring interacting with the alkali is slightly deformed towards a trapezium. The Al–Al bond interacting with the alkali shrinks, the opposite Al–Al bond (R2(X) in Table 3) remains similar, while the perpendicular Al–Al

Table 3. Properties of the alkaliized $X[Al_4MAI_4]^-$ complexes. Definition of the structural parameters are given in Figure 3. The reported values are obtained at the B3LYP/6-311+G* level of theory. Distances are given in Å, and NICS in ppm. Index (X) indicates the Al_4 ring interacting with the alkali.

| X | $X[Al_4TiAl_4]^-$ | | | $X[Al_4ZrAl_4]^-$ | | | $X[Al_4HfAl_4]^-$ | | |
|--------------|-------------------|-------|--------|-------------------|--------|--------|-------------------|--------|--------|
| | Li | Na | K | Li | Na | K | Li | Na | K |
| R1 | 2.701 | 2.707 | 2.713 | 2.672 | 2.683 | 2.672 | 2.664 | 2.683 | 2.608 |
| R2 | 2.719 | 2.715 | 2.725 | 2.740 | 2.739 | 2.746 | 2.742 | 2.741 | 2.759 |
| R1(X) | 2.704 | 2.727 | 2.726 | 2.690 | 2.707 | 2.686 | 2.677 | 2.708 | 2.591 |
| R2(X) | 2.746 | 2.720 | 2.730 | 2.811 | 2.793 | 2.815 | 2.841 | 2.801 | 2.868 |
| R3(X) | 2.629 | 2.641 | 2.662 | 2.632 | 2.657 | 2.665 | 2.635 | 2.655 | 2.669 |
| R_{C-M} | 1.971 | 1.974 | 1.917 | 2.112 | 2.167 | 2.172 | 2.178 | 2.085 | 2.227 |
| $R_{C(X)-M}$ | 1.934 | 1.931 | 1.894 | 2.124 | 2.112 | 2.119 | 2.133 | 2.122 | 2.198 |
| R_{X-Al} | 2.690 | 3.033 | 3.434 | 2.703 | 3.038 | 3.442 | 2.691 | 3.033 | 3.483 |
| planarity | 2.2 | 2.5 | 2.6 | 2.6 | 3.03 | 2.9 | 2.7 | 3.46 | 4.7 |
| planarity(X) | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| β | 155.6 | 155.2 | 157.6 | 153.1 | 153.4 | 154.0 | 151.7 | 152.31 | 157.15 |
| α | 134.2 | 127.0 | 130.2 | 122.0 | 116.9 | 111.8 | 119.8 | 114.72 | 71.03 |
| NICS(0) | -38.02 | -18.5 | -24.22 | -20.76 | -18.64 | -13.43 | -14.08 | -12.22 | 1.70 |
| NICS(1) | -15.02 | -12.1 | -14.0 | -14.55 | -13.25 | -12.38 | -11.33 | -11.20 | -2.74 |
| NICS(0)(X) | -27.37 | -36.9 | -35.99 | -24.42 | -24.57 | -22.78 | -18.49 | -18.36 | -2.63 |
| NICS(1)(X) | -16.18 | -15.9 | -15.6 | -14.42 | -14.53 | -17.28 | -11.70 | -11.23 | -1.75 |

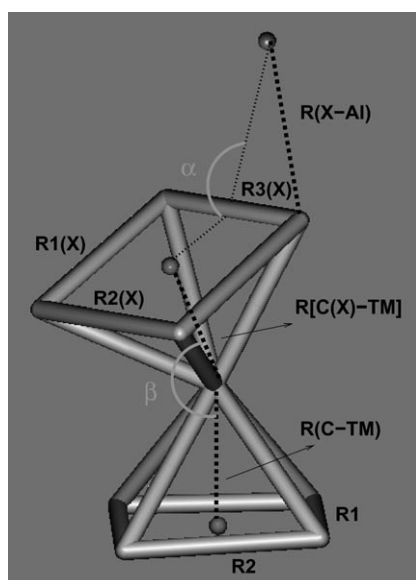


Figure 3. $X[Al_4MAI_4]^-$ ground state structure of the alkaliized sandwich complexes ($M=Ti, Zr,$ and Hf). The dots within the squares indicate the centres of gravity of aluminum rings and the uppermost dot denotes the alkali metal ($X=Li, Na$ and K).

bond ($R1(X)$) shrinks. The opposite aluminum ring also gets slightly distorted, acquiring a rhomboidic shape.

Overall, the different alkali cations do not yield sizeable changes to the geometry of both aluminum rings of the sandwich complex. Similar deformations have also been reported for a bare Al_4^{2-} ring upon interaction with alkali

ions.^[1,14] Despite of the geometrical distortion, the planarity of the Al_4 ring that interacts with the alkali is maintained, while it is slightly broken in the opposite ring. This loss of planarity is larger in the Hf sandwich (especially upon interaction with potassium, for which the planarity is lost by almost 5°; see planarity values in Table 3).

In spite of the fact that the aluminum square rings are slightly distorted after the alkali addition, overall their NICS properties remain similar. This indicates that the aromaticity of the aluminum rings remains upon interaction with the alkali cation in all these complexes, as shown in Table 3. The largest

change observed occurred on the $K[Al_4HfAl_4]^-$ complex, for which the NICS values are significantly more positive, suggesting substantial reduction of the aromaticity for this complex. In particular, the NICS(0) value becomes positive, hence the σ aromaticity is lost in the aluminum ring that does not interact directly with K^+ . The addition of an alkali atom lowers the complex charge from 2- to 1- and also renders the complex more stable toward electron detachment. Thus, the EDE's of the alkaliized complexes are now all positive as shown in Table 4.

However, the geometrical distortion induced by the alkali cation may shed some doubts about the stability of the resulting structure towards fragmentation. Although one can envisage a number of fragmentation reactions, we have chosen reaction (1), in which the XAl_6^- cluster is taken as reference because it has been found to be particularly stable.^[15] The ΔE 's and ΔG 's of reaction (1) are collected in Table 5.

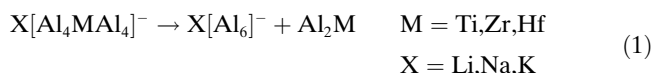


Table 4. Electron detachment energies, in eV, for the $X[Al_4MAI_4]^-$ complexes.

| X | $X[Al_4TiAl_4]^-$ | | | $X[Al_4ZrAl_4]^-$ | | | $X[Al_4HfAl_4]^-$ | | |
|----------------|-------------------|-------|-------|-------------------|-------|-------|-------------------|-------|-------|
| | Li | Na | K | Li | Na | K | Li | Na | K |
| VGF^{HOMO} | [a] | 1.450 | [a] | 1.910 | 1.843 | 1.552 | 1.836 | 1.545 | 1.437 |
| pole strength | - | 0.891 | - | 0.904 | 0.901 | 0.909 | 0.899 | 0.889 | 0.894 |
| VGF^{HOMO-1} | 1.792 | 2.256 | 1.811 | 1.619 | 1.491 | 1.323 | 1.711 | 1.841 | 1.539 |
| pole strength | 0.911 | 0.887 | 0.906 | 0.913 | 0.914 | 0.928 | 0.893 | 0.882 | 0.883 |
| VGF^{HOMO-2} | 2.344 | 2.642 | 1.566 | 2.571 | 2.613 | 2.397 | 2.594 | 2.595 | 2.235 |
| pole strength | 0.916 | 0.860 | 0.914 | 0.892 | 0.889 | 0.890 | 0.889 | 0.880 | 0.873 |
| VGF^{HOMO-3} | 1.241 | 2.180 | 2.085 | 2.552 | 2.375 | 2.208 | 2.579 | 2.615 | 2.366 |
| pole strength | 0.953 | 0.879 | 0.922 | 0.865 | 0.865 | 0.869 | 0.883 | 0.870 | 0.871 |
| VGF^{HOMO-4} | 1.830 | 2.779 | [a] | 2.620 | 2.562 | 2.361 | 2.483 | 2.450 | 2.264 |
| pole strength | 0.894 | 0.910 | - | 0.890 | 0.880 | 0.885 | 0.854 | 0.862 | 0.867 |

[a] The outer valence approximation did not converge due to the small pole strength.

Table 5. Fragmentation energies for reaction (1) of the different X-[Al_qMAI₄]^{q-} sandwiches. Energies are in kcal mol⁻¹ and the free energies are calculated at 298 K.

| X | Ti | | Zr | | Hf | |
|----|--------|--------|--------|--------|--------|--------|
| | ΔE | ΔG | ΔE | ΔG | ΔE | ΔG |
| Li | -42.21 | -32.33 | -51.15 | -40.95 | -45.71 | -35.48 |
| Na | -46.64 | -36.92 | -55.81 | -45.63 | -50.09 | -39.97 |
| K | -48.04 | -38.45 | -57.07 | -47.35 | -52.02 | -40.25 |

The large negative values of the ΔG's suggest that the complexes are more stable than the separated fragments, which is supportive of the stabilization imparted by the counterion to the complexes.

Conclusion

We have characterized the structures and the properties of the [Al_qMAI₄]^{q-} (q=2, 1, 0 and M=Ti, V, Cr, Zr, Nb, Ta, Mo, Hf, Ta, and W) sandwich complexes. The Ti, Zr, and Hf complexes have a charge of 2-; the V, Nb, and Ta complexes 1-; and the Cr, Mo, and W complexes are neutral. All these sandwich complexes are minima in their potential-energy surfaces and have similar structures. The most sizeable structural difference found between the different sandwiches is the distance from the transition metal to the tetraaluminum rings, which decreases as the total charge of the complex is reduced.

Various properties have been analyzed to determine the stability of the sandwiches. Only the sandwich complexes with a 2- charge have certain instabilities, due the fact that the electron-detachment energies of these sandwiches are negative, indicating a propensity towards spontaneous electron detachment, given that the barrier for such an electron ejection process is expected to be small.

Nevertheless, the 2- complexes can be stabilized by the addition of an appropriate counterion. We found that Li⁺, Na⁺, and K⁺ cations do stabilize the complexes. These cations interact with the aluminum rings rather than with the transition metal. The mode of interaction of the cations and the aluminum rings parallels that found for the bare Al₄²⁻. The alkali cation bends the sandwich complexes, but keeps all other structural properties of the complex nearly unchanged.

Once the sandwiches are formed, the geometric features of both Al₄²⁻ units remain essentially unaltered, as do the aromatic properties of the aluminum rings. The loss of the σ aromaticity of the aluminum ring not interacting with the alkali cation of the K[Al₄HfAl₄]⁻ complex is the sole remarkable aromatic effect induced by the counterion.

Acknowledgements

This research was funded by Euskal Herriko Unibertsitatea (the University of the Basque Country), Gipuzkoako Foru Aldundia (the Provincial

Government of Guipuzkoa), Eusko Jaurlaritz (the Basque Government) and the Swedish Science Research Council (VR). The SGI/IZO-SGIker UPV/EHU (supported by the National Program for the Promotion of Human Resources within the National Plan of Scientific Research, Development and Innovation—Fondo Social Europeo and MCyT) is gratefully acknowledged for assistance and generous allocation of computational resources.

- [1] X. Li, A. E. Kuznetsov, H. F. Zhang, A. I. Boldyrev, L.-S. Wang, *Science* **2001**, *291*, 859.
- [2] A. I. Boldyrev, L. S. Wang, *Chem. Rev.* **2005**, *105*, 3716.
- [3] C.-G. Zhan, F. Zheng, D. A. Dixon, *J. Am. Chem. Soc.* **2002**, *124*, 14795.
- [4] A. E. Kuznetsov, A. I. Boldyrev, *Struct. Chem.* **2002**, *13*, 141.
- [5] J. Chandrasekhar, E. D. Jemmis, P. von R. Schleyer, *Tetrahedron Lett.* **1979**, *20*, 3707.
- [6] M. Unverzagt, G. Subramanian, M. Hofmann, P. v. R. Schleyer, S. Berger, K. Harms, W. Massa, A. Berndt, *Angew. Chem.* **1997**, *109*, 1567; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1469.
- [7] C. Präsang, A. Młodzianowska, Y. Sahin, M. Hofmann, G. Geiseler, W. Massa, A. Berndt, *Angew. Chem.* **2002**, *114*, 3529; *Angew. Chem. Int. Ed.* **2002**, *41*, 3380.
- [8] C. Corminboeuf, C. S. Wannere, D. Roy, R. B. King, P. von R. Schleyer, *Inorg. Chem.* **2006**, *45*, 214.
- [9] A. E. Kuznetsov, A. I. Boldyrev, X. Li, L.-S. Wang, *J. Am. Chem. Soc.* **2001**, *123*, 8825.
- [10] X. Li, H.-F. Zhang, L.-S. Wang, A. E. Kuznetsov, N. A. Cannon, A. I. Boldyrev, *Angew. Chem.* **2001**, *113*, 1919; *Angew. Chem. Int. Ed.* **2001**, *40*, 1867.
- [11] J. Jusélius, M. Straka, D. Sundholm, *J. Phys. Chem. A* **2001**, *105*, 9939.
- [12] P. W. Fowler, R. W. A. Havenith, E. Steiner, *Chem. Phys. Lett.* **2002**, *359*, 530.
- [13] A. E. Kuznetsov, K. A. Birch, A. I. Boldyrev, X. Li, H.-J. Zhai, L.-S. Wang, *Science* **2003**, *300*, 622.
- [14] A. I. Boldyrev, A. E. Kuznetsov, *Inorg. Chem.* **2002**, *41*, 532.
- [15] A. E. Kuznetsov, A. I. Boldyrev, H.-J. Zhai, X. Li, L.-S. Wang, *J. Am. Chem. Soc.* **2002**, *124*, 11791.
- [16] J. M. Mercero, J. M. Ugalde, *J. Am. Chem. Soc.* **2004**, *126*, 3380.
- [17] A. Datta, S. K. Pati, *J. Am. Chem. Soc.* **2005**, *127*, 3496.
- [18] Gaussian03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford, CT, **2004**.
- [19] J. M. Mercero, J. M. Matxain, X. Lopez, D. M. York, A. Largo, L. A. Eriksson, J. M. Ugalde, *Int. J. Mass Spectrom.* **2005**, *240*, 37.
- [20] M. Dolg, H. Stoll, H. Preuss, R. Pitzer, *J. Phys. Chem.* **1993**, *97*, 5852.
- [21] A. Dhavale, D. G. Kanhere, S. A. Blundell, R. R. Zope, *Phys. Rev. B* **2002**, *65*, 085402.
- [22] V. I. Minkin, M. N. Glukovtsev, B. Y. Simkin, *Aromaticity and Antiaromaticity*, Wiley, New York, **1994**.
- [23] Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. von R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842.

- [24] Z. Cheng, C. Corminboeuf, T. Heine, J. Bohmann, P. von R. Schleyer, *J. Am. Chem. Soc.* **2003**, *125*, 13930.
- [25] Y. Jung, T. Heine, P. von R. Schleyer, M. Head-Gordon, *J. Am. Chem. Soc.* **2004**, *126*, 3132.
- [26] A. C. Tsipis, C. A. Tsipis, *J. Am. Chem. Soc.* **2003**, *125*, 1136.
- [27] C. A. Tsipis, E. E. Karagiannis, P. F. Kladou, A. C. Tsipis, *J. Am. Chem. Soc.* **2004**, *126*, 12916.
- [28] X. Huang, H. J. Zhai, B. Kiran, L. S. Wang, *Angew. Chem.* **2005**, *117*, 7417; *Angew. Chem. Int. Ed.* **2005**, *44*, 7251.
- [29] G. Schaftenaar, J. H. Noordik, *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123–134.
- [30] D_{4d} symmetry structures of Zr, Nb, Mo, Ta and W showed a small imaginary frequency (less than 20 cm). Lower symmetry structures were found to be minima with a very small (negligible) difference in the geometries.
- [31] R. W. A. Havenith, J. H. van Lenthe, *Chem. Phys. Lett.* **2004**, *385*, 198.
- [32] J. M. Mercero, J. M. Matxain, J. M. Ugalde, *Angew. Chem.* **2004**, *116*, 5601; *Angew. Chem. Int. Ed.* **2004**, *43*, 5485.

Received: January 24, 2006