



MOLECULAR STRUCTURE MODELS OF Al_2Ti_3 AND Al_2V_3 CLUSTERS ACCORDING TO DFT QUANTUM-CHEMICAL CALCULATIONS

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Basic parameters of molecular structures of Al_2Ti_3 and Al_2V_3 metal clusters (bond lengths, bond angles, and torsion (dihedral) angles), have been calculated using DFT method at the OPBE/QZVP level. It has been shown that the Al_2Ti_3 cluster may exist in 14 modifications and Al_2V_3 in 11 ones, differing noticeably in their total energy. Besides, the molecular structures of these metal clusters differ significantly in terms of geometric parameters as well as in external form. Moreover, the most energetically stable modifications of Al_2Ti_3 and Al_2V_3 clusters differ each other considerably in geometric form also.

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INTRODUCTION

Earlier quantum chemical calculations of a number of heterobimetallic metal clusters containing atoms of various *p*- and *d*-elements^{1–18} has been carried out using the density functional theory (DFT) method. Some of such metal clusters have been applied in various fields of science and technology.^{10–14} In the works cited above, the objects of study were the so-called (*dd*) heterobimetallic metal clusters, which included atoms of two different *d*-elements, namely (Cu, Fe),¹ (Pd, Fe),² (Pd, Ag),^{3–5} (Pt, Cu),⁶ (Au, Fe),⁷ (Au, Pd)⁸ and (Au, Ag).⁹ However, of no less interesting are the (*pd*) heterobimetallic metal clusters that include atoms of different categories of metals, namely, *p*- and *d*-elements, since theoretically it can be expected that they will demonstrate such new properties that are not inherent of metal clusters containing metal atoms of only one category.

Among the most important *p*-elements is aluminum, which has a very wide industrial application. Nevertheless, only a few (*pd*) metal clusters containing this *p*-element and any of *d*-metals are described in the literature.^{15–18} On the one hand, such metal clusters can serve as efficient catalysts for a number of sol–gel technology processes that occur in inorganic as well as in organic silicate media. On the other hand, they can play the role of specific “precursors” for the production of micro- and nano-particles of metal oxides and metal chalcogenides, that, in turn, are very convenient starting materials for the creation of various composite materials. Previously^{16–21} we have carried out quantum chemical calculations, using the DFT method, of molecular structures of four different (*pd*) metal clusters with the Al_2M_3 composition ($M = Cr, Mn, Fe, Co, Ni, Cu, Zn$) and showed that each of them exists in various modifications. Besides, the number of such modifications varies from 8 in

the case of $Fe^{17,19}$ and $Cu^{19,20}$ to 25 in the case of Mn^{21} . On the other hand, it seems reasonable to see how, with the same formal stoichiometric composition of Al_2M_3 , the nature of another *3d*-metal affects the number of possible modifications of the corresponding metal cluster and their relative stability. Taking into account this circumstance, as well as the fact that the Al_2M_3 metal clusters for $M = Cr, Mn, Fe, Co, Ni, Cu, Zn$ have already been studied by us,^{16–21} metal clusters having the same stoichiometric composition Al_2M_3 but containing Ti and V as a *3d*-metal, were selected as the objects of this study. These two elements are the first two members of a group of *3d*-elements (electronic configurations are $4s^23d^1$ and $4s^23d^2$, respectively), and calculations of metal clusters of the Al_2M_3 type by DFT method has not yet been carried out for them. In view of this, this investigation is devoted to the identification of possible modifications of metal clusters of Al_2Ti_3 and Al_2V_3 composition, the calculation of the basic parameters of their structures [metal-metal bond lengths, bond and torsion (dihedral) angles] and relative stability of these modifications from an energy point of view.

CALCULATION METHODS

The quantum-chemical calculations of Al_2Ti_3 and Al_2V_3 metal clusters were carried out using the density functional method (DFT) combining the standard extended split-valence QZVP basis^{22,23} and the OPBE functional.^{24,25} The data of previous works^{26–29} give us reason to assert that the given method allows to obtain the most accurate estimation of ratio between energies of the high-spin state and low-spin state and, at the same time, rather reliably predicts the key geometric parameters of molecular structures for various compounds of *3p*- and *3d*-elements. To build quantum chemical models of the molecular structures of the metal clusters under examination, GAUSSIAN09 software was used.³⁰ As before,^{16–21} the accordance of the found stationary points to the energy minima was confirmed by calculation of the second derivatives with respect to the atomic coordinates. Besides, all equilibrium structures corresponding to the minima at the potential energy surface revealed only real positive frequency values. Parameters of the molecular structures for spin multiplicities (M_s) more than 1, were

determined using the so-called unrestricted method (UOPBE) and for $M_S = 1$, using the so-called restricted method (ROPBE). Along with this, the unrestricted method in conjunction with the GUESS = Mix option was used for the cases when M_S was equal to 1. The data, obtained as a result of such a procedure, are similar to those obtained using ROPBE method.

RESULTS AND DISCUSSION

According to results of DFT quantum-chemical calculation of Al_2Ti_3 and Al_2V_3 metal clusters, 14 forms of cluster Al_2Ti_3 and 11 forms of cluster Al_2V_3 are capable to autonomous existence. Molecular structures of Al_2Ti_3 cluster are presented in **Figure 1**. Relative total energies of these structures are given in table 1. As may be seen from these data, only half of the 14 modifications of Al_2Ti_3 , namely Al_2Ti_3 (I), Al_2Ti_3 (II), Al_2Ti_3 (IV), Al_2Ti_3 (V), Al_2Ti_3 (VII), Al_2Ti_3 (VIII) and Al_2Ti_3 (X), contain a covalent Al–Al bond, in the other seven Al_2Ti_3 structures, there are only the Ti–Ti and Ti–Al bonds.

Table 1. Relative total energies of different structures of the Al_2Ti_3 clusters.

Structure symbol	Spin multiplicity of ground state	Relative total energy, kJ mol^{-1}	Number of chemical bonds in the structure		
			Al–Al	Al–Ti	Ti–Ti
Al_2Ti_3 (I)	3	80.9	1	6	2
Al_2Ti_3 (II)	1	24.1	1	6	2
Al_2Ti_3 (III)	1	93.0	0	6	2
Al_2Ti_3 (IV)	5	60.7	1	6	1
Al_2Ti_3 (V)	5	19.7	1	5	2
Al_2Ti_3 (VI)	3	37.2	0	5	3
Al_2Ti_3 (VII)	1	44.8	1	5	3
Al_2Ti_3 (VIII)	1	77.5	1	5	3
Al_2Ti_3 (IX)	5	73.0	0	6	1
Al_2Ti_3 (X)	3	37.0	1	6	2
Al_2Ti_3 (XI)	5	0.0	0	6	3
Al_2Ti_3 (XII)	3	12.6	0	6	3
Al_2Ti_3 (XIII)	1	21.5	0	6	3
Al_2Ti_3 (XIV)	1	51.1	0	6	3

From the information contained in it clearly follows that the most stable in total energy is the modification of Al_2Ti_3 (XI), having a geometry of a trigonal bipyramid, in the “equatorial flatness” of which there are three titanium atoms, the atoms of aluminium are located at its vertices. The modification showing the next higher total energy, namely Al_2Ti_3 (XII), has a similar structure (Figure 1). It is interesting to note in this connection that in both these most stable modifications, Al–Al bond is absent. In most of the Al_2Ti_3 modifications, 10 out of 14, there are six Ti–Al bonds, and only in four of them, namely in Al_2Ti_3 (V)- Al_2Ti_3 (VIII), there are five. Complete set of Ti–Ti bonds, that is 3, occurs in seven structures, Al_2Ti_3 (VI)- Al_2Ti_3 (VIII), Al_2Ti_3 (XI)- Al_2Ti_3 (XIV); two such bonds are present in five modifications, Al_2Ti_3 (I)- Al_2Ti_3 (III), Al_2Ti_3 (V) and Al_2Ti_3 (X). Finally, in two modifications, Al_2Ti_3 (IV) and Al_2Ti_3 (IX) have one.

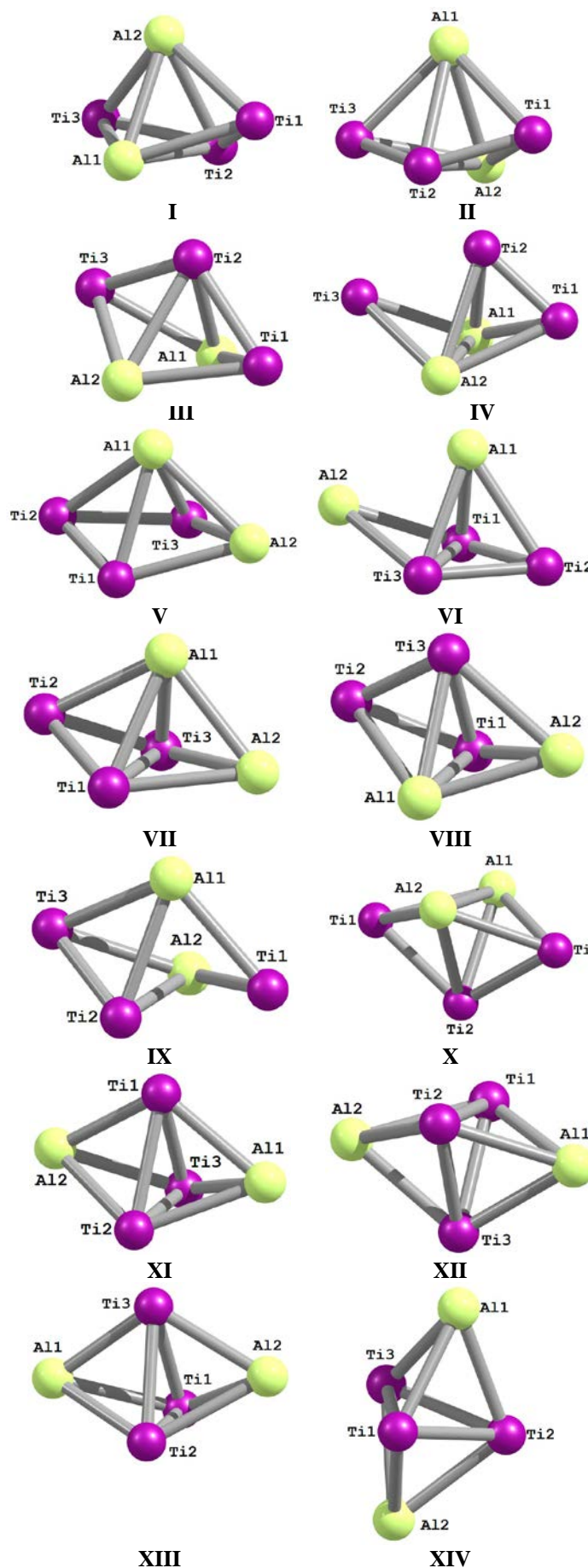


Figure 1. Molecular structures of Al_2Ti_3 clusters.

The most energetically favorable Al_2Ti_3 (XI) modification contains maximal possible number of Al–Ti and Ti–Ti bonds (6 and 3, respectively). On the whole, it can be stated that most of the modifications of the given metal cluster have the structure of a trigonal bipyramid or close to it. The exceptions are only Al_2Ti_3 (V) with a structure close to the tetragonal pyramid and also Al_2Ti_3 (IV), Al_2Ti_3 (VI) and Al_2Ti_3 (IX), which have the structure of a “cap” tetrahedron (Figure 1). The Ti–Ti bond lengths in Al_2Ti_3 metal clusters are in the ranges of 210–260 pm, and the lengths of the Al–Ti and Al–Al bonds are in the ranges of 252–270 nm and 255–280 nm, respectively, that taking into account the atomic radii of these elements, 143 pm for Al and 132 pm for Ti, seems quite natural and predictable.

Among all modifications of cluster under examination, four modifications, namely Al_2Ti_3 (IV), Al_2Ti_3 (V), Al_2Ti_3 (IX), and Al_2Ti_3 (XI), have $M_S = 5$, four, Al_2Ti_3 (I), Al_2Ti_3 (VI), Al_2Ti_3 (X), and Al_2Ti_3 (XII) have $M_S = 3$ and the other six have $M_S = 1$ (Table 1). It is noticed from these data that the last spin state for the given metal cluster is predominant. Nevertheless, in fairness, it should be noticed that the nearest in energy to the conformation Al_2Ti_3 (XI), Al_2Ti_3 (XII), and Al_2Ti_3 (V), with relative total energies 12.6 and 19.7 kJ mol^{-1} , respectively, have in the ground state $M_S = 3$ and $M_S = 5$, respectively (Table 1). The most high-energetic modification of the considered metal cluster, and namely Al_2Ti_3 (III), has relative total energy 93.0 kJ mol^{-1} and $M_S = 1$. It should be noted in this connection that the most stable modification of Al_2Ti_3 with $M_S = 1$, is Al_2Ti_3 (XIII) having relative total energy 21.5 kJ mol^{-1} (Table 1).

Nine oscillations, active in IR spectrum, should appear in a nonlinear five-atom molecule (to number of which belongs Al_2Ti_3) according to theoretical expectations. This quantity turns out to be correct in Al_2Ti_3 (XI) metal cluster according to our calculation (Table 2).

Table 2. The oscillation frequencies in most stable modification of Al_2Ti_3 (XI) cluster.

Oscillation frequency, cm^{-1}	Assignment of oscillation frequency
121	Wagging for Al1 and Al2 atoms relatively Ti1–Ti3 bond
154	Wagging for Al1 and Al2 atoms relatively Ti1–Ti2 bond
203	Scissoring for Ti1, Ti2, and Ti3 atoms
217	Stretching (<i>asym.</i>) for Al1 and Al2 atoms relatively Ti1 atom
237	Stretching (<i>asym.</i>) for Al1 and Al2 atoms relatively Ti1–Ti2 bond
250	Scissoring for Al1, Ti3, and Al2 atoms
263	Stretching (<i>sym.</i>) for Al1 and Al2 atoms relatively Ti3 atom
345	Stretching (<i>sym.</i>) for Al1, Ti3 and Al2, Ti3 atom pairs
350	Stretching (<i>sym.</i>) with participation of all atoms in Al_2Ti_3 metal cluster

Molecular structures of the various Al_2V_3 metal clusters are shown in Figure 2 and the relative total energies of them are given in the table 3. As may be seen from these data in six of 11 of these structures, the direct valence bond of Al–Al occurs, the exceptions are the structures of Al_2V_3 (VII)– Al_2V_3

(XI). Also, in most of the modifications of metal cluster under the study, excluding only Al_2V_3 (VIII) and Al_2V_3 (IX), there are at least one V–V bond. Nevertheless, in each of the modifications of Al_2V_3 , there are at least five Al–V bonds. It is noteworthy that in Al_2V_3 (VIII) and Al_2V_3 (IX) modifications mentioned above, there are only Al–V bonds (6 in the each of them). Besides, the most stable modification of this metal cluster, namely Al_2V_3 (V), contains 7 metal–metal bonds (Table 3).

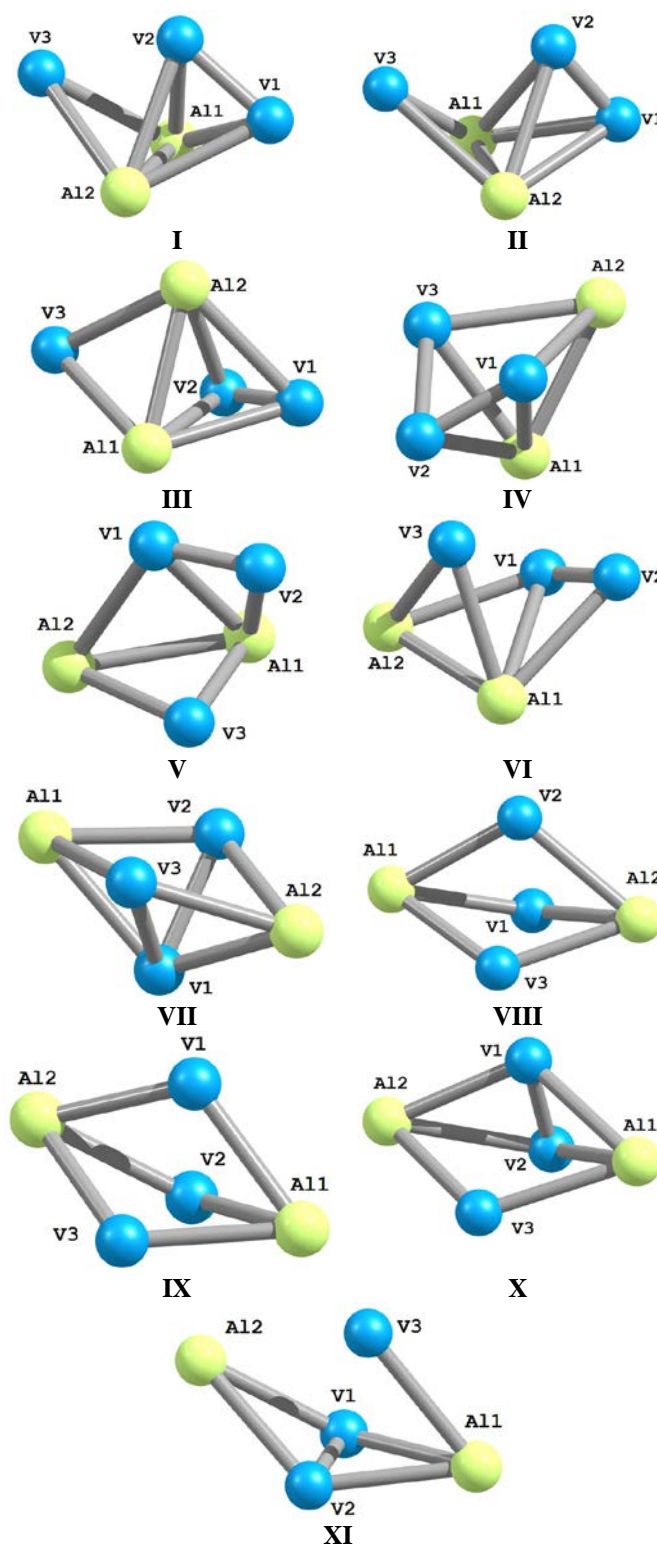


Figure 2. Molecular structures of Al_2V_3 clusters.

It should be noted especially that, on the whole, molecular structures of Al₂V₃ differ substantially from molecular structures of Al₂Ti₃, at that, not only by the number of metal-metal bonds, but, also, by its geometrical form (Figures 1 and 2).

As can be seen from the data of Table 3, the most stable modification, namely Al₂V₃ (V), has not the highest spin multiplicity (6), but a lower one (4). Besides, which is characteristic, the structures with the highest M_S = 6 generally have noticeably larger values of the total energies than those with multiplicities M_S = 2 and M_S = 4. It is characteristic that the Al₂V₃ (II) structure nearest to Al₂V₃ (V) in energy has the same spin multiplicity as Al₂V₃(V), and its molecular structure, at least in general terms, resembles Al₂V₃ (V). At the same time, the following three structures with increasing energy, namely Al₂V₃(III), Al₂V₃ (I) and Al₂V₃ (IV), have different M_S values, namely, 6, 2, and 2, respectively. The least stable in terms of energy is the modification of Al₂V₃ (IX), the total energy of which is not only much higher (by almost 150 kJ mol⁻¹) than that of Al₂V₃(V), but also of all the other modifications of the metal cluster under study. Remarkably, it has the highest spin multiplicity (6). The V–V bond lengths in the Al₂V₃ metal cluster considered here are in the 170–275 pm range, while the Al–V and Al–Al bond lengths are in the 250–270 nm and 255–270 nm ranges, respectively (Table 3). Taking into account the radii of the atoms of these elements, 143 pm for Al and 134 pm for V, it seems quite natural.

Table 3. Relative total energies of different structures of the Al₂V₃ clusters.

Structure symbol	Spin multiplicity of ground state	Relative total energy, kJ mol ⁻¹	Number of chemical bonds in the structure		
			Al–Al	Al–V	V–V
Al ₂ V ₃ (I)	2	25.9	1	6	1
Al ₂ V ₃ (II)	4	2.4	1	6	1
Al ₂ V ₃ (III)	6	18.8	1	6	1
Al ₂ V ₃ (IV)	2	26.7	1	5	2
Al ₂ V ₃ (V)	4	0.0	1	5	1
Al ₂ V ₃ (VI)	6	26.8	1	5	1
Al ₂ V ₃ (VII)	2	30.2	0	6	2
Al ₂ V ₃ (VIII)	4	71.3	0	6	0
Al ₂ V ₃ (IX)	6	141.0	0	6	0
Al ₂ V ₃ (X)	4	59.6	0	6	1
Al ₂ V ₃ (XI)	6	74.6	0	5	1

As in Al₂Ti₃ metal clusters, nine oscillations active in IR spectrum developed in Al₂V₃ ones also, according to our calculation. Frequencies of such oscillation for most stable modification of Al₂V₃, namely Al₂V₃ (V), are presented in table 4. It should be noted in this connection that, despite the same the total number of oscillations active in the IR spectra of the Al₂Ti₃ (XI) and Al₂V₃ (V) clusters, their characteristics differ very strongly from each other. It is enough to compare the range of frequencies that are active in the IR spectrum. In the case Al₂Ti₃ (XI), it is less than 250 cm⁻¹ (from 121 to 350 cm⁻¹), while in the case of Al₂V₃ (V) is almost 500 cm⁻¹ (from 96 to 586 cm⁻¹) i.e., almost twice as large. The values of these frequencies are also considerably different among themselves. At the same time, which is noteworthy, there are dissimilarities not only in

terms of the frequencies of these oscillations, but also in their nature. No close similarity between the frequencies of the metal clusters considered here and the composition of the metal clusters described previously,^{16–21} is found.

The general structural feature of both Al₂Ti₃ and Al₂V₃ metal clusters under examination, is the presence of several M–M bonds (M= Ti, V) formed by the same atom with its "neighbors" (Figures 1 and 2). On the average, the number of Al–Al, Al–M and M–M bonds in Al₂Ti₃ metal clusters, as can see by comparing figures 1 and 2, is somewhat more than in Al₂V₃ ones. At the same time, here, as well as in the metal clusters described earlier,^{16–21} the values of most of the bond angles and, also, torsion (dihedral) angles, are significantly lower than 90° (see Tables 1 and 3).

Table 4. The oscillation frequencies in most stable modification of Al₂V₃ (V) cluster.

Oscillation frequency, cm ⁻¹	Assignment of oscillation frequency
96	Scissoring for Al2 and V2 atoms relatively V1–V3 bond
175	Scissoring for Al2 and Al2 atoms relatively V1–V3 bond
189	Scissoring for V1, Al2 and V3 atoms
201	Superposition of scissoring oscillations of atoms V1, V2, V3 and atoms V1, V3, Al2
216	Stretching (<i>asym.</i>) for Al1–Al2 and Al1–V2 bonds
241	Stretching (<i>sym.</i>) for Al1–V1 and Al1–V2 bonds
271	Stretching (<i>asym.</i>) for Al1–V3 and Al2–V3 bonds
330	Stretching (<i>sym.</i>) for Al1–Al2, Al1–V3, and Al2–V3 bonds
586	Stretching for V1–V2 bond

There are many common features of the both Al₂Ti₃ and Al₂V₃ metal clusters studied by us. The most typical structure according to theoretical expectations, is a trigonal bipyramid. This is especially pronounced for Al₂Ti₃. At the same time, as is apparent from figures 1 and 2. A greater structural diversity is noted among Al₂V₃ metal clusters, although the total number of their modifications is less than the number of such modifications for Al₂Ti₃ metal clusters. All of them are also characterized by relatively high values of the lengths of these Al–Al, Al–M and M–M bonds, which, as a rule, exceed 200 pm almost in every case. The few exceptions to this rule are only V1–V2 bond lengths in the Al₂V₃ (I)–Al₂V₃(VI), Al₂V₃(X) and Al₂V₃(XI) structures, which lie in the range from 171.7 pm, in the Al₂V₃ (VI) to 188.1 pm, in the Al₂V₃ (I) (see Supporting Information). Curiously enough in the structures of Al₂Ti₃ metal clusters there is no such examples, although the radius of the Ti atom (132 pm) is even slightly smaller than the radius of the V atom (134 pm). The overwhelming majority of the aluminum-titanium and aluminum-vanadium metal clusters considered here, either has no symmetry elements at all, or has only one plane of symmetry. The only exception is the Al₂V₃ (IX) metal cluster, which has one axis of symmetry of the third order, three axes of symmetry of the second order, and, also, three planes of symmetry (Figure 2). The Al₂Mn₃ (XVIII) and Al₂Zn₃ (XIV) metal clusters described in our previous article²¹ have similar structures, but each of them

has three M–M bonds, which are absent in Al₂V₃ (**IX**). In this connection, we would like to note that this cluster has the highest energy among all the Al₂V₃ metal clusters.

The key structural parameters of most stable Al₂Ti₃ and Al₂V₃ metal clusters, and namely Al₂Ti₃ (**XI**) and Al₂V₃ (**V**), are presented in the table 5. As can be seen from it, the longest are Al–Al bonds, the shortest are Ti–Ti bonds. Similar situation, in average, occurs for both types of metal clusters under examination.

Table 5. Metal–metal bond lengths, bond and torsion angles in the molecular structures of most stable modifications of Al₂Ti₃ (**XI**) and Al₂V₃ (**V**) metal clusters.

Al ₂ Ti ₃ (XI)		Al ₂ V ₃ (V)	
Metal-metal bond lengths, pm*			
Al1Al2	(422.7)	Al1Al2	270.2
Al1Ti1	254.4	Al1V1	263.7
Al1Ti2	258.2	Al1V2	265.7
Al1Ti3	258.2	Al1V3	252.2
Al2Ti1	254.4	Al2V1	261.0
Al2Ti2	258.2	Al2V2	(378.8)
Al2Ti3	258.2	Al2V3	254.4
Ti1Ti3	258.7	V1V3	(265.4)
Ti2Ti3	239.0	V2V3	(253.3)
Ti1Ti2	258.8	V1V2	171.7
Bond angles, deg **			
Ti1Al1Ti2	60.6	V1Al1V2	37.8
Ti1Al2Ti2	60.6	V1Al2V2	(22.9)
Ti1Al1Al2	(33.8)	V1Al1Al2	58.5
Ti1Al2Al1	(33.8)	V1Al2Al1	59.5
Ti2Al1Al2	(35.6)	V2Al1Al2	90.0
Ti2Al2Al1	(35.0)	V2Al2Al1	(44.5)
Al1Ti1Al2	112.3	Al1V1Al2	62.0
Al1Ti2Al2	109.9	Al1V2Al2	(45.5)
Al1Ti3Al2	109.9	Al1V3Al2	64.5
Ti1Al1Ti3	60.6	V1Al1V3	(61.9)
Ti1Al2Ti3	60.6	V1Al2V3	62.0
Ti1Ti3Ti2	62.5	V1V3V2	(38.6)
Ti2Al1Ti3	55.1	V2Al1V3	58.5
Ti2Al2Ti3	55.1	V2Al2V3	(41.6)
Ti1Ti2Ti3	62.5	V1V2V3	(74.5)
Torsion (dihedral) angles, deg ***			
Ti1Al2Al1Ti3	(-126.2)	V1Al2Al1V3	74.3
Ti2Al2Al1Ti3	(107.4)	V2Al2Al1V3	(52.1)
Ti1Ti3Ti2Al1	-67.4	V1V3V2Al1	(-76.3)
Ti1Ti3Ti2Al2	-67.4	V1V3V2Al2	(-19.1)
Ti1Al1Al2Ti2	(-126.4)	V1Al1Al2V2	(-22.3)
Ti1Ti2Al1Al2	(-31.0)	V1V2Al1Al2	-31.8
Ti1Ti2Al2Al1	(31.0)	V1V2Al2Al1	-31.8
Ti2Ti3Al2Al1	(41.9)	V2V3Al2Al1	(56.4)

In this table in brackets are shown * = distances between two atoms not involved in chemical bonds, ** = angles formed by three atoms among which at least two atoms do not form chemical bonds, and *** = dihedral angles formed by four atoms among which at least two atoms do not form chemical bonds are parenthesized.

Taking into account the atomic radii of the chemical elements contained in Al₂M₃ metal clusters considered here, Al 143 pm, Ti 132 pm and V 134 pm, the indicated ratio between these bond lengths seems quite normal. Since the radii of titanium and vanadium atoms differ among themselves only slightly, one would expect that, in average, M–M bonds in the metal clusters considered here, should be close to each other. The data of our calculation, in general, are in accordance with this expectation (see Supporting Information).

When characterizing the spin multiplicity of the ground state of the most stable modifications of each of these metal clusters, we would like to stress the following. Despite the fact that the low-spin state for both of them as a whole, judging by the data of tables 2 and 4, is less characteristic compared to high-spin, the latter is realized only in the case of the most stable aluminum-titanium metal cluster of Al₂Ti₃ (**XI**). At the same time, for the most stable aluminum-vanadium metal cluster of Al₂V₃ (**V**), the ground state has spin multiplicity which is an intermediate between the minimum and the maximum value of the spin multiplicity. By taking into consideration the electron configurations of the titanium and vanadium atoms (3d²4s² and 3d³4s², respectively), this tendency is quite expected.

CONCLUSION

As can be seen from the calculated data presented above, the five-atomic metal clusters Al₂Ti₃ and Al₂V₃ under study, form a fairly significant number of structural modifications, that differ significantly from one another in their structural geometrical parameters and in terms of total energies. In addition, the number of modifications of both the one and the other metal cluster (14 and 11, respectively) exceeds the number of modifications of the Al₂Fe₃ metal cluster²⁰ (of which there are only 8), but turns out to be much smaller than the number of modifications of Al₂Mn₃, 25.²¹ Most of the modifications of these metal clusters, both Al₂Ti₃ and Al₂V₃, either have no symmetry elements at all, or have only one plane of symmetry. Moreover, in the modifications of Al₂Ti₃ metal cluster, as a rule, each of the aluminum and titanium atoms in their composition, has been connected through chemical bonds to its three neighbors, whereas in the modifications of Al₂V₃ one, this is manifested to a considerably lesser degree. It is noteworthy that the lowest-energetic modification in the case of Al₂Ti₃ has a spin multiplicity of the ground state 5, in the case of Al₂V₃ it is 4, although judging by the electronic configurations of the atoms in them (3s²3p¹, 4s²3d¹ and 4s²3d², respectively), the total number of unpaired electrons in Al₂Ti₃ should be less than in Al₂V₃. Besides, the difference between the energies of the lowest-energy and the highest-energy modifications in the case of Al₂V₃ (141.0 kJ mol⁻¹) was significantly larger than in the case of Al₂Ti₃ (93.0 kJ mol⁻¹), although much less than in the case of a metal cluster Al₂Fe₃, where it exceeds 300 kJ mol⁻¹.²⁰

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