Polyhedral Ionic Molecules

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Abstract: Small isolated clusters of alkali halides and analogous divalent species composed of closed-shell atomic ions are known to prefer densely packed structures similar but not identical to the repeat units found in the solid state. Beyond the simple cube structure that occurs, for example, in alkali halide tetramers, no other ionic polyhedral structures containing only atomic ions are known. In this article, we explore the possibility of other three-dimensional structures, and we show computationally that two molecules, $Mg_2Al_4O_8$ and $Na_4Mg_4O_6$, have very stable distorted rhombic dodecahedron structures. We therefore suggest that a wide variety of stable polyhedral structures could be constructed from ions, and we offer a simple electrostatic model for predicting which polyhedral ionic structures should be stable and which should not. We point out that several recently observed inorganic solid state materials contain core structures that fit our predictions.

I. Introduction

Polyhedral compounds have long aroused fascination among chemists because of the symmetric harmony existing within these molecules. Although beautiful and easy to visualize, polyhedral structures have presented long-standing synthetic challenges, e.g., the syntheses of tetrahendrane,[1] prizmane,[2] octahedrane,[3] cubane,[4] dodecahedrane,[5] and C_{60},[6] attracted much attention in the chemistry community.

Most common polyhedral molecules are composed of main group elements that can assume two or more valence states or coordination numbers (e.g., beryllium, boron, carbon, phosphorus, and their valence analogs) and do not contain ionic or highly polar bonding. The only known polyhedral molecules built from atomic ions are the monoionic tetramers A^+B^- of alkali halides (e.g., Li^+F^-) and the diionic tetramers $A^{2+}B^{2-}$ of alkaline earth oxides (e.g., $Mg^{2+}O^{2-}$), both of which have cube shapes.[7] These cluster molecules are not as energetically stable as their bulk ionic crystals, but their vapors can be detected and spectroscopically characterized in equilibrium with the ionic solids at high temperatures. It is in this sense that such neutral polyhedral clusters built from ionic fragments are viewed as stable molecular clusters.

Beyond the tetramers, larger molecular clusters composed of atomic ions usually have three-dimensional (3D) lattice structures similar to those occurring in the corresponding bulk solid states.[8] However, the results obtained in this work and presented here lead us to suggest that another geometrical possibility exists for building stable polyhedral molecules from atomic ions. If these predictions are correct, such new cluster molecules should be observable in vapors in equilibrium with bulk solids or formed via laser ablation.

In the present article, we present a simple electrostatic model that can be used to guide construction of polyhedral ionic molecules, and we offer results of our ab initio calculations on specific cases to support the validity of this model.

II. Theoretical Model for Polyhedral Ionic Molecules

Let us assume that polyhedral ionic molecules are to be constructed from closed-shell atomic ions that can be of charge ±1, ±2, etc. (e.g., Li^+, F^-, Mg^{2+}, or O^{2-}). Before moving on to treat fully 3D structures, let us begin by considering the planar analogs of polyhedral molecules—polygons. Within such polygons, the close location of two positive or two negative ions would be energetically disfavored. Therefore, to attain the most stable situation, the charges of the ions should alter as one moves along any closed path of neighboring ions within the polygon. An immediate result is that only polygons with an even number of edges will be energetically favored. For example, the rhombus, square, and hexagon all have an even number of edges, so negative ions can be located between positive ions and vice versa. In triangles, pentagons, etc. (with an odd number of edges), at least two ions of the same sign must be located close to each other, which will destabilize these structures. This simple Coulomb-repulsion argument forms the basis of the model that we exploit below to suggest stoichiometries and structures for the new polyhedral molecules promised in the abstract. The construction rule based on Coulomb repulsions is analogous to rules that emphasize avoiding odd-numbered rings in $(BN)_n$ compounds because two neighboring N atoms can be eliminated to produce N_2 in a likely exothermic event.

For planar polygon clusters, does this simple model work? Indeed the rhombus or nearly square structures are found in nature for $(LiF)_2$ and $(MgO)_2$, and hexagon structures are known to be the global minima for $(LiF)_3$ and $(MgO)_3$. For 3D

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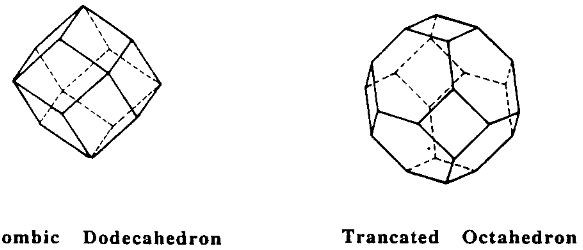

Figure 1. Rhombic dodecahedron and truncated octahedron.

polyhedral structures of ionic molecules, we therefore propose a similar construction rule: *only structures where all closed paths among neighboring ions have an even number of edges will be stable*. Based on this rule, one could exclude many of the highly symmetric Platonic solids: the tetrahedron, octahedron, icosohedron, and dodecahedron. Each of these structures contains closed paths containing three or five edges and therefore would have two neighboring ions of the same sign. The highly popular C_{60} type structure also does not satisfy the charge alternation rule because it has internal pentagon closed paths. Only one Platonic solid, the cube, is a polyhedral structure satisfying the charge alternation construction rule. In a cube, all possible closed paths have an even number of edges; therefore positive and negative ions can occupy alternating sites.

What occurs in nature for 3D clusters? It is well-known that both LiF and MgO tetramers have cubic structures,[7,8] in agreement with the charge alternation rule. In recent ab initio theoretical studies of $(NaCl)_n$ clusters, Ochsenfeld and Ahlrichs[8c] examined the $n = 1-6$, 8, 9, 12, 15, 18, and 32 systems. They concluded that the energetically most stable isomers of even the smaller clusters $n \geq 4$ show a marked preference for geometries that are fragments of the rock salt solid state lattice. Structures containing high-symmetry polyhedrons were not found in their research except for the cube in the $n = 4$ case.

It appears from the earlier theoretical work cited above as well as from what is known experimentally that the simple cube is the only convex polyhedron that mother nature has made (can make?) from atomic ion building blocks. However, by examining the charge alternation construction rule in more detail and trusting it to predict energetically favored structures, we are led to believe that, for appropriate selections of atomic ions, other new convex polyhedron structures are possible for ionic molecules. We decided to use the rule to predict a convex polyhedral structure larger than the cube and to then test its predicted stability by carrying out ab initio calculations on it. The polyhedron which has only even numbered closed paths that we selected is the rhombic dodecahedron presented in Figure 1.

III. Predicted Stoichiometry for the Rhombic Dodecahedron

One can see from Figure 1 that a rhombic dodecahedron has two distinct types of vertices: six vertices (S) have four closest neighbors and eight vertices (E) have three closest neighbors. As is the focus of this paper, we wish to create a neutral molecule that uses closed-shell atomic ions. There are two possibilities: we can place the positive ions at the S positions and the negative ions at E positions; alternatively, we can place the cations at S and the anions at E. For the anions, we choose oxides, because oxygen is known to occupy stable 4-fold sites, for example, in the center of the square structure of Al_4O.[9]

If we place the O^{2-} anions in the eight E positions, to make a neutral molecule we must select a *mixture* of *doubly*- and *triply*-charged positive ions to occupy the six S positions and thus cancel the 16 negative charges from the eight O^{2-} ions. We could, for example, select Al^{3+} ions for the triply positive ions and Mg^{2+} for the doubly charged anions and place them at the six S positions, in which case we find that we must use four Al^{3+} ions and two Mg^{2+} ions. Thus, we predict the stoichiometry for this rhombic dodecahedron molecule to be $Mg_2Al_4O_8$.

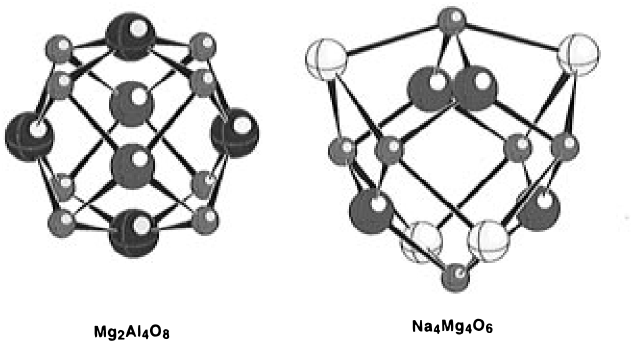

Figure 2. Optimized global minimum structure for $Mg_2Al_4O_8$ and $Na_4Mg_4O_6$ (O, red; Na, yellow; Mg, blue; Al, green).

In the alternative case described above, we can place six doubly-charged O^{2-} ions at the six S positions. To make a neutral molecule we must select a *mixture* of *singly*- and *doubly*-charged positive ions to cancel the 12 negative charges from the O^{2-}. If we select Na^+ and Mg^{2+} ions and place them at the eight E positions we predict a stoichiometry for such a rhombic dodecahedron molecule to be $Na_4Mg_4O_6$.

Although $Mg_2Al_4O_8$ and $Na_4Mg_4O_6$ obey the charge alternation rule when the ions occupy the rhombic dodecahedron, are these polyhedral clusters really stable? To address this question, we performed full geometry optimization for both molecules using ab initio self-consistent field (SCF), Møller–Plesset second-order perturbation theory (MP2), and density functional theory (DFT/B3LYP) methods and split-valence 6-31+G* basis sets, and we performed local harmonic vibrational frequency calculations at the SCF/6-31+G* and B3LYP/6-31+G* levels all within the GAUSSIAN 94 program.[10] The resulting optimal structures are shown in Figure 2, and their unique interionic distances and effective atomic charges within the Natural Population Analysis are given in Table 1. The vibrational frequencies and corresponding IR intencities are presented in Table 2. Indeed, we found that both structures are true minima on their respective ground state potential energy surfaces, although the fully optimized structures are not perfect rhombic dodecahedrons; the Mg–O bonds are shorter than the Na–O bonds in $Na_4Mg_4O_6$ and the Al–O bonds shorter than the Mg-O bonds in $Mg_2Al_4O_8$.

We also examined other characteristics of the two polyhedral clusters predicted here. Our calculated atomic charges (using Weinhold's bond order[12] natural population analysis) show that

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Table 1. Calculated Molecular Properties for the Rhombic Dodecahedron Structures of $Na_4Mg_4O_6$ and $Mg_2Al_4O_8$[a]

method	SCF/6-31+G*	B3LYP/6-31+G*	MP2/6-31+G*
	$Na_4Mg_4O_6$ (T_d, $^1A_1$)		
R(Mg−O), Å	1.906	1.924	1.947
R(Na−O), Å	2.370	2.388	2.443
R(O−O), Å	3.155	3.194	3.234
R(Mg−Mg), Å	3.021	3.029	3.056
R(Mg−Na), Å	2.797	2.812	2.877
Q^{NBO}(Mg)	+1.83	+1.78	+1.74
Q^{NBO}(Na)	+0.97	+0.95	+0.94
Q^{NBO}(O)	−1.86	−1.82	−1.79
	$Mg_2Al_4O_8$ (D_{4h}, $^1A_{1g}$)		
R(Al−O), Å	1.826	1.853	1.867
R(Mg−O), Å	2.015	2.034	2.049
R(O−O), Å	2.400	2.447	2.468
R(Al−Al), Å	2.553	2.571	2.585
R(Mg−Mg), Å	4.243	4.270	4.300
Q^{NBO}(Mg)	+1.87	+1.83	+1.81
Q^{NBO}(Al)	+2.20	+2.06	+2.00
Q^{NBO}(O)	−1.57	−1.49	−1.45

[a] Only closest distances are presented.

both molecules are essentially ionic (see Q values in Table 1). Both molecules have high HOMO-LUMO energy gaps (9.3 eV for $Na_4Mg_4O_6$ and 10.4 eV for $Mg_2Al_4O_8$), so they are expected to display the stability to reactivity characteristic of closed-shell molecules. Our calculated dissociation energies of $Na_4Mg_4O_6$ into 4MgO + $2Na_2O$ and of $Mg_2Al_4O_8$ into 2MgO + $2Al_2O_3$ were found to be 628 (642) and 466 (467) kcal/mol, respectively, at the MP2/6-31+G* and B3LYP/6-31+G* levels, the latter given in parentheses. Therefore both of these molecules are expected to be very thermochemically stable. Ionization potentials are also useful for identification of molecules in the gas phase; our calculated vertical electron detachment energies (VEDE) for both molecules at the PMP2/6-31+G* level were found to be: VEDE = 7.56 ($Na_4Mg_4O_6$) and 8.12 eV ($Mg_2Al_4O_8$).

Because of the large number of atoms in both of the above molecules, it is very difficult to *prove* via ab initio methods that the rhombic dodecahedron structures are the true global minima; there are simply too many alternative structures whose energies must be computed to make this feasible. However, even if the structures predicted above are only local minima, we believe they could be experimentally identified with matrix isolation techniques or in the gas phase. If the rhombic dodecahedrons are global minima, they probably could be made by the simple "shake and bake" synthetic methods.

Recently, there have been three experimental findings that lend further support to our suggestion that polyhedral structures may exist as especially stable species even when formed from ionic fragments. A distorted rhombic dodecahedron was identified[13] as the $Li_4\ Al_4\ P_6$ "core" within the $[Li(OC_4\ H_8\ )]_4$-$[\{(AlMe)[\mu\text{-}P(C_6H_{11})]\}_2\{\mu\text{-}P(C_6\ H_{11}\ )\}]_2C_6H_5Me$ solid. An analogous $Li_4\ Sn_4\ P_6$ core has been found[14] in $[\{Sn_2(PC_6H_{11})_3\}_2$-$Li_44thf]2thf\}]$; and a $Yb_6\ I_8$ core was identified[15] in $[\{Yb_6[\eta\text{-}C_5Me_4(SiMe_2Bu^t)]_6I_8\}\{Li(thf)_4\}_2]$. Although all there of these cases involve solid-state species, they support the notion of the special stability of the particular polyhedral structures proposed by us.

Table 2. Calculated Frequencies (IR Intensities in km/mol Are in Parentheses) for the Rhombic Dodecahedron Structures of $Na_4Mg_4O_6$ and $Mg_2Al_4O_8$

	SCF/6-31+G*	B3LYP/6-31+G*
	$Na_4Mg_4O_6$ (T_d, $^1A_1$)	$Na_4Mg_4O_6$ (T_d, $^1A_1$)
$\nu_1(a_1)$, cm^{-1}	550.9 (0.0)	492.3 (0.0)
$\nu_2(a_1)$, cm^{-1}	411.9 (0.0)	375.7 (0.0)
$\nu_3(a_1)$, cm^{-1}	239.7 (0.0)	223.2 (0.0)
$\nu_4(e)$, cm^{-1}	616.9 (0.0)	581.4 (0.0)
$\nu_5(e)$, cm^{-1}	227.7 (0.0)	213.0 (0.0)
$\nu_6(e)$, cm^{-1}	140.0 (0.0)	122.4 (0.0)
$\nu_7(t_1)$, cm^{-1}	631.4 (0.0)	597.9 (0.0)
$\nu_8(t_1)$, cm^{-1}	283.8 (0.0)	256.3 (0.0)
$\nu_9(t_1)$, cm^{-1}	219.8 (0.0)	192.0 (0.0)
$\nu_{10}(t_2)$, cm^{-1}	682.2 (668.0)	638.2 (453.3)
$\nu_{11}(t_2)$, cm^{-1}	554.8 (52.8)	516.7 (32.6)
$\nu_{12}(t_2)$, cm^{-1}	414.2 (22.2)	362.9 (12.4)
$\nu_{13}(t_2)$, cm^{-1}	316.5 (262.9)	292.0 (211.3)
$\nu_{14}(t_2)$, cm^{-1}	217.5 (3.2)	204.4 (1.0)
$\nu_{15}(t_2)$, cm^{-1}	187.4 (19.1)	170.6 (18.1)
	$Mg_2Al_4O_8$ (D_{4h}, $^1A_{1g}$)	$Mg_2Al_4O_8$ (D_{4h}, $^1A_{1g}$)
$\nu_1(a_{1g})$, cm^{-1}	760.7 (0.0)	677.3 (0.0)
$\nu_2(a_{1g})$, cm^{-1}	670.6 (0.0)	581.8 (0.0)
$\nu_3(a_{1g})$, cm^{-1}	541.3 (0.0)	502.5 (0.0)
$\nu_4(a_{1g})$, cm^{-1}	366.4 (0.0)	333.2 (0.0)
$\nu_5(a_{2g})$, cm^{-1}	570.4 (0.0)	525.4 (0.0)
$\nu_6(a_{1u})$, cm^{-1}	289.4 (0.0)	266.5 (0.0)
$\nu_7(a_{2u})$, cm^{-1}	814.6 (1280.6)	736.8 (837.6)
$\nu_8(a_{2u})$, cm^{-1}	569.1 (10.2)	517.7 (15.2)
$\nu_9(a_{2u})$, cm^{-1}	445.3 (189.6)	403.9 (145.4)
$\nu_{10}(b_{1g})$, cm^{-1}	722.4 (0.0)	645.8 (0.0)
$\nu_{11}(b_{1g})$, cm^{-1}	335.5 (0.0)	308.6 (0.0)
$\nu_{12}(b_{2g})$, cm^{-1}	761.8 (0.0)	700.8 (0.0)
$\nu_{13}(b_{2g})$, cm^{-1}	633.4 (0.0)	572.6 (0.0)
$\nu_{14}(b_{2g})$, cm^{-1}	275.3 (0.0)	259.5 (0.0)
$\nu_{15}(b_{1u})$, cm^{-1}	434.3 (0.0)	407.3 (0.0)
$\nu_{16}(b_{1u})$, cm^{-1}	236.8 (0.0)	227.5 (0.0)
$\nu_{17}(b_{2u})$, cm^{-1}	673.4 (0.0)	619.6 (0.0)
$\nu_{18}(b_{2u})$, cm^{-1}	363.6 (0.0)	328.0 (0.0)
$\nu_{19}(e_g)$, cm^{-1}	667.9 (0.0)	612.8 (0.0)
$\nu_{20}(e_g)$, cm^{-1}	573.2 (0.0)	525.2 (0.0)
$\nu_{21}(e_g)$, cm^{-1}	448.2 (0.0)	421.1 (0.0)
$\nu_{22}(e_g)$, cm^{-1}	282.3 (0.0)	262.6 (0.0)
$\nu_{23}(e_u)$, cm^{-1}	773.6 (845.0)	706.8 (544.6)
$\nu_{24}(e_u)$, cm^{-1}	723.9 (206.5)	651.4 (147.7)
$\nu_{25}(e_u)$, cm^{-1}	603.6 (116.2)	556.0 (71.1)
$\nu_{26}(e_u)$, cm^{-1}	518.1 (142.5)	464.7 (98.1)
$\nu_{27}(e_u)$, cm^{-1}	338.2 (6.1)	313.9 (3.4)

IV. Remarks on Other Polyhedral Ionic Molecules

Further experimental verification of the molecules predicted here by us is eagerly anticipated. If it appears that our predictions are correct, as our ab initio data and the solid-state structural findings[13−15] suggest, we look forward to studying other larger polyhedral ionic molecules such as the truncated octahedron shown in Figure 1, which also satisfies the construction rule because it is composed of squares and hexagons.

Moreover, there are other clusters that have already been made that can be viewed in terms of the model proposed here and that lend support to this model. A whole class of ionic molecules known as Met-Cars has recently been experimentally discovered.[11] While the structures of these molecules are not yet known, Castleman and co-authors[11a,b] *proposed* a dodecahedron structure (Figure 3) for their Met-Cars. At first glance, such structures do not seem to fit our construction rule. However, realizing that Met-Cars contain the molecular-anion structural unit C_2^{2-}, and postulating that our rules for *atomic* ions can be generalized to molecular ions (e.g., by identifying C_2^{2-} as analogous to O^{2-}), the Met-Car's proposed dodecahedral structure does indeed follow our simple electrostatic model. Of course, because C_2^{2-} is now identified as the anionic building block unit, and taking into account that in the dodecahedral

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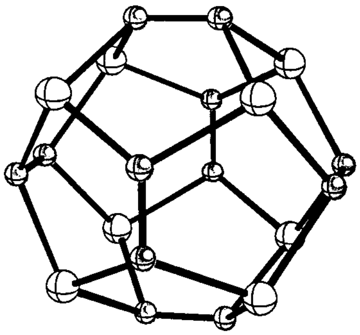

Ti_8C_{12}

Figure 3. Dodechahedron structure proposed for Ti_8C_{12} Met-Car (ref 11a, b).

structure one C_2^{2-} group will form an edge and another will contribute only one carbon atom to the face, our rules must be generalized to state that each closed path must have an *odd* number of edges (as does the Met-Car's proposed dodecahedral structure).

Based on the predictions given earlier and using the $O^{2-} \rightarrow C_2^{2-}$ replacement deemed appropriate to Met-Cars, we suggest that a particularly interesting species to study would be $Na_4Mg_4C_{12}$. Finally, if the polyhedral structures discussed here are deep local minima, they may suggest a route to forming multiply charged anions in the gas phase. For example, if one replaces two aluminum ions by magnesium ions in $Mg_2Al_4O_8$ or two magnesium ions by sodium ions in $Na_4Mg_4O_6$, one obtains two dianions, $Mg_4Al_2O_8^{2-}$ and $Na_6Mg_2O_6^{2-}$, respectively, which we found both to be minima and to possess negative highest occupied molecules orbitals −1.3 and −0.3 eV, respectively, at SCF/6-31+G* level of theory. Therefore both dianions are electronically stable at the Koopmans' theorem level, but additional calculations need to be made to make a final conclusion. We believe that polyhedral structures could be very common for ionic molecules, and we hope that this article will provoke extensive research in this field.

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