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LETTERS

Peculiar Structures of Small Magnesium Carbide Clusters: MgC_2, $(MgC_2)_2$, and $(MgC_2)_4$

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The geometries of MgC_2, $(MgC_2)_2$, and $(MgC_2)_4$ in their ground and low-lying excited electronic states have been determined via ab initio electronic structure methods with flexible basis sets and using various approaches for treating electron correlation. We find these species to involve primarily ionic bonding and to be very thermodynamically stable. We find the C_2^{2-} moiety to exhibit both 1- and 2-fold coordination to the Mg^{2+} sites in the two larger clusters, which is reminiscent of what is seen in transition metal met-car compounds.

Recently we predicted[1] that $Mg_2Al_4O_8$ and $Na_4Mg_4O_6$ have distorted rhombic dodecahedron structures that are thermodynamically very stable, and we proposed a simple electrostatic model for predicting a wide variety of such stable polyhedral structures that are built from atomic or small molecular ions.

In the present Letter, we extend our earlier study to ionic clusters composed of magnesium ions and molecular C_2^{2-} ions, in particular to species in which the C_2^{2-} moiety can be coordinated either to one or to two counterions (i.e., in a linear or side on geometry). Similar coordination possibilities for C_2^{2-} have been suggested to occur in the new class of species known as Met-Cars that have the formula M_8C_{12} (M = Ti, V, Zr, Hf, Fe, Cr, and Mo).[2-6] Specifically, Castleman et al.[2-4] proposed a pentagonal dodecahedral cage structure for the Met-Cars in which each of the pentagonal faces contains three C atoms and two M atoms. Both to extend our earlier work on three-dimensional clusters containing Mg atoms and to further examine cases where C_2^{2-} coordinates in both 1- and 2-fold ways, we decided to study the title cluster compounds.

The geometries of MgC_2, $(MgC_2)_2$, and $(MgC_2)_4$ were optimized employing analytical gradients with polarized split-valence basis sets (6-31+G*) at the SCF levels and at the DFT (B3LYP) levels of theory. The most stable resulting structures were then reoptimized at the MP2/6-31+G* level. The MgC_2 geometry was further reoptimized at the MP2(full)/6-311+G* and at QCISD/6-311+G* levels of theory. The optimized geometries were then used to perform energy calculations at the QCISD(T)/6-311+G(2df) level for MgC_2 and at the QCISD(T)/6-311+G* level for $(MgC_2)_2$. The fundamental vibrational frequencies, normal coordinates, and zero-point energies (ZPE) were calculated by standard FG matrix methods within the Gaussian 94 program.[7]

In the remainder of this Letter, we present results only for the most stable structures of MgC_2, $(MgC_2)_2$, and $(MgC_2)_4$; we will present the results of our extensive investigations of other low-energy structures in a subsequent full paper, which will include a comprehensive study of the intramolecular rearrangements of these molecules, results of our search for the global-minimum structures including a wide variety of tentative structures, and the multiplicities and ionization potentials for all molecules examined. Our results for the lowest energy structures of MgC_2, $(MgC_2)_2$, and $(MgC_2)_4$ are summarized in Table 1 and Figure 1.

MgC_2

For MgC_2, we studied singlet, triplet, and quintet structures within both a linear MgCC and a T-shaped bridged coordination of the CC group to the Mg atom. The singlet T-shaped structure (C_{2v}, $^1A_1$, see Table 1 and Figure 1) was found to be the global minimum, and the geometries at the SCF/6-31+G*, B3LYP/6-31+G*, and MP2/6-31+G* levels (Figure 1) are very similar to those at the MP2(full)/6-311+G* (R(Mg−C) = 2.012 Å and (R(C−C) = 1.291 Å) and QCISD/6-311+G* (R(Mg−C) =

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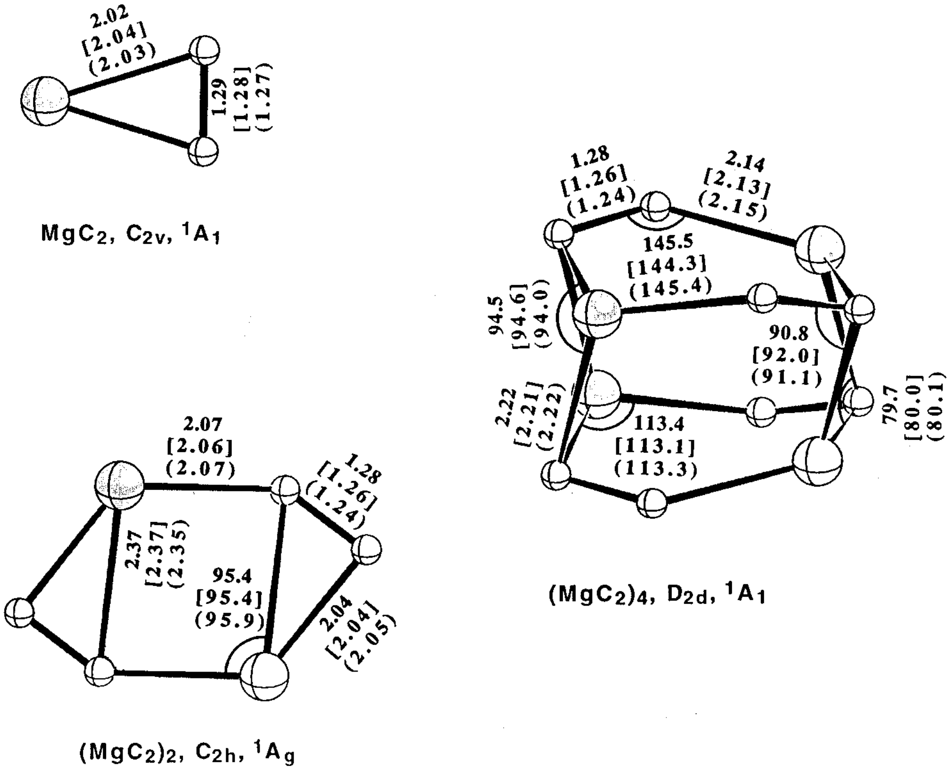

Figure 1. Optimized global minimum structure for MgC_2, $(MgC_2)_2$, and $(MgC_2)_4$ at the MP2/6-31+G* level (numbers in parentheses at the SCF/6-31+G* level and numbers in brackets at B3LYP/6-31+G* level). Bond lengths and valence angles are in angstroms and degrees, respectively.

TABLE 1: Calculated Molecular Properties of the Lowest Molecular Structures of MgC_2, $(MgC_2)_2$, and $(MgC_2)_4$

	SCF	B3LYP	MP2		SCF	B3LYP	MP2
			MgC_2 (C_{2v}, $^1A_1$)				
E_{tot}, au	−275.154 082	−276.125 073	−275.438 990	Q^{Mull}(Mg)	+0.63	+0.51	+0.56
$\nu_1(a_1)$, cm^{-1}	1886.7 (129.3)	1762.9 (2.1)	1690.6 (2.8)	Q^{Mull}(C)	−0.31	−0.25	−0.28
$\nu_2(a_1)$, cm^{-1}	630.2 (59.1)	594.0 (13.3)	650.5 (68.3)	Q^{NBO}(Mg)	+1.47	+1.22	+1.30
$\nu_3(b_2)$, cm^{-1}	383.7 (7.9)	390.5 (2.7)	445.2 (6.2)	Q^{NBO}(C)	−0.73	−0.61	−0.65
			$(MgC_2)_2$ (C_{2h}, ^1A_g)				
E_{tot}, au	−550.529 354	−552.444 874	−551.086 461	$\nu_{10}(b_u)$, cm^{-1}	633.1 (354.3)	623.2 (270.1)	638.7 (278.8)
$\nu_1(a_g)$, cm^{-1}	2094.8 (0.0)	1933.9 (0.0)	1831.8 (0.0)	$\nu_{11}(b_u)$, cm^{-1}	497.5 (127.9)	489.8 (73.8)	496.1 (84.2)
$\nu_2(a_g)$, cm^{-1}	586.1 (0.0)	585.1 (0.0)	609.9 (0.0)	$\nu_{12}(b_u)$, cm^{-1}	263.4 (151.0)	242.9 (128.5)	258.4 (162.5)
$\nu_3(a_g)$, cm^{-1}	532.0 (0.0)	516.3 (0.0)	515.8 (0.0)	Q^{Mull}(Mg)	+0.57	+0.43	+0.60
$\nu_4(a_g)$, cm^{-1}	303.0 (0.0)	283.5 (0.0)	289.3 (0.0)	Q^{Mull}(C_b)	−0.14	+0.37	+0.12
$\nu_5(a_g)$, cm^{-1}	218.1 (0.0)	206.1 (0.0)	217.1 (0.0)	Q^{Mull}(C_t)	−0.43	−0.80	−0.72
$\nu_6(a_u)$, cm^{-1}	242.4 (116.1)	228.4 (86.9)	225.4 (97.6)	Q^{NBO}(Mg)	+1.71	+1.60	+1.62
$\nu_7(a_u)$, cm^{-1}	145.1 (63.7)	138.6 (53.7)	128.6 (54.3)	Q^{NBO}(C_b)	−1.01	−0.94	−0.93
$\nu_8(b_g)$, cm^{-1}	208.5 (0.0)	205.5 (0.0)	189.8 (0.0)	Q^{NBO}(C_t)	−0.70	−0.66	−0.68
$\nu_9(b_u)$, cm^{-1}	2097.0 (70.7)	1938.4 (45.9)	1836.1 (43.5)				
			$(MgC_2)_4$ (D_{2d}, $^1A_1$)				
E_{tot}, au	−1101.222 664	−1105.043 471	−1102.343 776	$\nu_{15}(b_2)$, cm^{-1}	297.5 (94.9)	286.8 (78.1)	
$\nu_1(a_1)$, cm^{-1}	2098.5 (0.0)	1935.3 (0.0)		$\nu_{16}(b_2)$, cm^{-1}	194.8 (23.7)	180.9 (29.9)	
$\nu_2(a_1)$, cm^{-1}	487.5 (0.0)	488.1 (0.0)		$\nu_{17}(e)$, cm^{-1}	2098.9 (16.1)	1936.5 (8.5)	
$\nu_3(a_1)$, cm^{-1}	444.5 (0.0)	438.4 (0.0)		$\nu_{18}(e)$, cm^{-1}	482.4 (319.6)	477.6 (274.3)	
$\nu_4(a_1)$, cm^{-1}	328.7 (0.0)	312.5 (0.0)		$\nu_{19}(e)$, cm^{-1}	436.9 (100.2)	439.3 (48.4)	
$\nu_5(a_1)$, cm^{-1}	274.2 (0.0)	256.1 (0.0)		$\nu_{20}(e)$, cm^{-1}	377.0 (113.2)	377.8 (97.7)	
$\nu_6(a_1)$, cm^{-1}	168.6 (0.0)	164.3 (0.0)		$\nu_{21}(e)$, cm^{-1}	284.8 (0.8)	268.8 (0.4)	
$\nu_7(a_2)$, cm^{-1}	305.6 (0.0)	310.0 (0.0)		$\nu_{22}(e)$, cm^{-1}	222.0 (32.6)	207.2 (37.9)	
$\nu_8(a_2)$, cm^{-1}	216.9 (0.0)	204.6 (0.0)		$\nu_{23}(e)$, cm^{-1}	103.2 (1.7)	94.4 (1.4)	
$\nu_9(b_1)$, cm^{-1}	322.6 (0.0)	324.3 (0.0)		Q^{Mull}(Mg)	+1.26	+0.66	+1.18
$\nu_{10}(b_1)$, cm^{-1}	317.5 (0.0)	299.8 (0.0)		Q^{Mull}(C_{bb})	−1.01	−0.90	−1.21
$\nu_{11}(b_1)$, cm^{-1}	73.2 (0.0)	59.7 (0.0)		Q^{Mull}(C_b)	−0.25	+0.23	+0.03
$\nu_{12}(b_2)$, cm^{-1}	2100.6 (0.6)	1938.5 (0.9)		Q^{NBO}(Mg)	+1.74	+1.67	+1.67
$\nu_{13}(b_2)$, cm^{-1}	506.9 (307.9)	500.6 (236.1)		Q^{NBO}(C_{bb})	−0.95	−0.92	−0.90
$\nu_{14}(b_2)$, cm^{-1}	463.1 (1.8)	459.9 (5.8)		Q^{NBO}(C_b)	−0.78	−0.75	−0.77

2.090 Å and (R(C−C) = 1.277 Å) levels. We believe that similar agreement can be expected for $(MgC_2)_2$ and $(MgC_2)_4$.

The singlet linear ($C_{\infty v}$, $^1\Sigma^+$) MgCC structure and the triplet T-structure (C_{2v}, $^3A_1$) are higher in energy than the most stable structure by 8.3 and 13.4 kcal/mol (all at the QCISD(T)/6-311+G(2df)//QCISD/6-311+G* level), respectively. The singlet T-structure is also very stable toward dissociation: $D_e(MgC_2 \rightarrow Mg+C_2)$ = 80.1 kcal/mol (at the QCISD(T)/6-311+G(2dt)//QCISD/6-311+G* level).

Our findings also suggest that Mg carbides have a lot in common with the corresponding oxides.[8] For example, the effective atomic charges for MgO, Q^{NBO}(Mg) = +1.41 at SCF/

6-311+G* and $Q^{NBO}(Mg) = +1.40$ at MP2(full)/6-311+G* [8]), and for MgC_2, $Q^{NBO}(Mg) = +1.47$ at SCF/6-311+G* and $Q^{NBO}(Mg) = +1.30$ at MP2(full)/6-311+G* (Table 1) are very similar, and for both molecules, the charge distributions are closer to $Mg^{1+}O^{1-}$ and $Mg^{1+}(C_2)^{1-}$ than to $Mg^{+2}O^{2-}$ and $Mg^{2+}C_2^{2-}$. The dissociation energies are also similar: $D_e(MgO) = 56.9$ kcal/mol and $D_e(MgC_2) = 80.1$ kcal/mol, as are lowest singlet−triplet splittings: $\Delta E^{S-T}(MgO) = 0.235$ eV (experiment 0.326 eV[9]) and $\Delta E^{S-T}(MgC_2) = 0.581$ eV (all at the QCISD(T)6-311+G(2df)//QCISD/6-311+G* level).

$(MgC_2)_2$

Recently[8] we studied the evolution of the charge distributions in $(MgO)_n$ going from the monomer to the tetramer and to the crystal. For $(MgC_2)_2$ we also studied a wide variety of singlet structures, which will be discussed in detail in our future comprehensive article. We found the singlet C_{2h} (^1A_g, see Table 1 and Figure 1) structure to be the global minimum at SCF/6-31+G*, B3LYP/6-31+G*, and MP2/6-31+G* levels of theory. We excluded triplet structures from consideration because MgC_2 has a singlet ground state and because we have seen for MgO and $(MgO)_2$[8] that the lowest triplet state moves to higher energy as the cluster size grows. In this most stable structure of $(MgC_2)_2$, the magnesium atoms are involved in both σ- and π-type coordination with the CC groups. Other structures containing only σ-type or only π-type coordination are found to be less stable.

The T-shape of the MgC_2 monomer unit is easily recognizable in the $C_{2h}(^1A_g)$ structure of the $(MgC_2)_2$ dimer. The main deformation inside the dimer involves the magnesium-bridged carbon bond whose length is elongated by 0.3 Å. The two types of carbons (bridged and terminal) have significantly different effective atomic charges, and the NBO atomic charges in the dimer are larger than those in the monomer, which is in agreement with what we found[8] for MgO and Mg_2O_2. Finally, the dimerization energy $(MgC_2)_2 \rightarrow 2MgC_2$ is 121.0 kcal/mol (at the QCISD(T)/6-311+G*//MP2/6-31+G* level), which is similar to the dimerization energy of MgO ($\Delta E = 125.1$ kcal/mol at the QCISD(T)/6-311+G(2df)//MP2(full)/6-311+G* [8] level of theory). Thus $(MgC_2)_2$ should be an extremely stable species.

$(MgC_2)_4$

For $(MgC_2)_4$, we also studied a wide variety of singlet structures which will be discussed in detail in our future comprehensive article. We found that the D_{2d} ($^1A_1$, see Table 1 and Figure 1) singlet structure is the global minimum at both the SCF/6-31+G* and B3LYP/6-31+G* levels of theory (the frequencies could not be calculated at the MP2/6-31+G* level of theory due to limited computing resources).

The tetramer $(MgC_2)_4$ has a very compact three-dimensional structure in which every C_2 group has two distinct carbon atoms; one is coordinated to one magnesium atom, while the other is coordinated to two magnesium atoms. In the latter case, the carbon atoms have a similar coordination environment to those in the pentagonal dodecahedral cage structure proposed by Castleman et al.[2−4] for Met-Cars. In $(MgC_2)_4$, the calculated C−C bond length is almost the same as in the dimer, but all of the Mg−C bonds are substantially longer. The effective atomic charges of the magnesium atoms and the doubly bridged carbon atoms in the tetramer are substantially larger than those in the monomer and dimer, which is in agreement with the trend found for MgO, Mg_2O_2 and Mg_4O_4.[8]

The dimerization energy of $(MgC_2)_2$ to form $(MgC_2)_4$ is 107.2 kcal/mol (at the MP2/6-31+G*//MP2/6-31+G* level), which is similar to the dimerization energy of $(MgO)_2$ ($\Delta E = 159$ kcal/mol at MP2/6-311+G*//MP2/6-311+G* [8]). The energy gain per Mg atom upon formation of $(MgC_2)_4$ from MgC_2 is 92.2 kcal/mol (at the MP2/6-31+G*//MP2/6-31+G* level).

In summary, we find in our ab initio calculations on MgC_2, $(MgC_2)_2$, and $(MgC_2)_4$ structures that are very thermodynamically stable, some of which involve 1- and 2-fold coordination of the C_2^{2-} moiety.

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