

Structural Characteristics of Small Magnesium Dichloride Clusters: A Systematic Theoretical Study

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The structures of small magnesium dichloride clusters were studied by ab initio quantum chemical methods. A technique was developed to take all conceivable structural isomers systematically into account. Altogether 168 isomers of $(\text{MgCl}_2)_n$, where $n = 1-4$, were optimized, from which data structural characteristics were determined. Generally, magnesium prefers coordination numbers of 3 and higher. Planar 3-coordinated and tetrahedral 4-coordinated orientations are particularly favored. The most stable isomer of the series of compounds studied, the one possessing tetrahedral 4-coordinated magnesium atoms, resembles a fragment of the magnesium dichloride lattice. On the basis of this tetramer, higher oligomers up to nonamers were studied, demonstrating the convergence of $(\text{MgCl}_2)_n$ clusters to the bulk structure of MgCl_2 .

Introduction

Magnesium dichloride is commonly used in industrial applications such as a catalyst support in Ziegler–Natta olefin polymerization catalysis.¹ The solid-state structure of magnesium dichloride is well known. There are three distinct crystalline forms: The most common is α with a rhombohedral structure.² The β form of MgCl_2 has a hexagonal close-packed structure,³ whereas the δ form is a rotationally disordered version of β magnesium dichloride.⁴ MgCl_2 crystals prefer coordination numbers of $n_c(\text{Mg}) = 6$ and $n_c(\text{Cl}) = 3$.

Rather little is known experimentally about the small magnesium dichloride clusters. The structures of the monomer,^{5–10} MgCl_2 , and dimer,^{5,9,10} Mg_2Cl_4 , have been experimentally studied. The MgCl_2 monomer is a linear molecule with $D_{\infty h}$ symmetry, and the dimer has a four-membered planar Mg_2Cl_2 ring with two bridging and two terminal chlorines, which results in D_{2h} symmetry. Structural parameters are available for the monomer and dimer.⁹

Although experimental data on magnesium dichloride species from the trimer to the bulk structure is unavailable, theoretical work has been carried out for the larger clusters. Axten et al.¹¹ have studied the structure of a D_{2d} -symmetric trimer (Mg_3Cl_6) by the Hartree–Fock method. The cluster prefers coordination numbers of 4 and 2 for Mg and Cl, respectively. An extensive study of larger magnesium dichloride clusters has been reported by Eichkorn et al.,¹² who considered larger clusters, including rings and lattice fragment structures.

In the present work, the structures of small $(\text{MgCl}_2)_n$ clusters were systematically screened in a search for the possible convergence of the clusters to the crystal structure of MgCl_2 . A technique was developed to generate all possible isomers of the clusters. Although chemical intuition, combined with the knowledge of similar types of SiS_2 structures,¹² would reduce the number of relevant structures for MgCl_2 clusters, this approach could not be applied to molecular systems in general. The systematic approach allowed us to verify that all structures, whether they are relevant or not, were taken into account.

TABLE 1: Number of $(\text{MgCl}_2)_n$ Isomers, $n = 1-4$

n	theoretical	optimized	minima (HF/3-21G*)	minima (MP2/6-311G*)
1	1	1	1	1
2	6	6	2	2
3	139	110	10	9
4	thousands	51	10	8

Therefore, the developed systematic methodology is also applicable to systems for which chemical knowledge is limited. Ab initio molecular orbital calculations were then performed to determine the preferred structural characteristics and relative stabilities for $(\text{MgCl}_2)_n$ clusters where $n = 1-4$. Higher oligomers were produced from these data.

Computational Details

The possible isomers of $(\text{MgCl}_2)_n$ are easy to elaborate when $n = 1-2$. However, raising n just to 3 or 4 increases the number of theoretical isomers dramatically. The systematic construction of all isomers then becomes troublesome, even for small $(\text{MgCl}_2)_n$ clusters.

A mathematical technique for generating every conceivable initial geometry of $(\text{MgCl}_2)_n$ clusters was developed and is presented in Supporting Information. The technique is based on a procedure in which isomers are built up from smaller substructures by the systematic addition of bridging and terminal atoms. The numbers of theoretical isomers are presented in Table 1. For the $(\text{MgCl}_2)_3$ cluster, 139 structural isomers are found, whereas for the $(\text{MgCl}_2)_4$ cluster the number of possible isomers increases to several thousand.

All theoretical isomers of the $(\text{MgCl}_2)_3$ cluster were investigated, excluding those with 1-coordinated magnesium. This exclusion reduced the number of isomers from 139 to 110. In the case of the $(\text{MgCl}_2)_4$ cluster, there were several thousand isomers, and straightforward modeling of each structure was not considered practical. Accordingly, a few geometrical restrictions, based on the results from smaller clusters, were applied to the initial structures: (1) Addition of the MgCl_2 fragment was made only to the most stable isomer of $(\text{MgCl}_2)_3$. (2) The objective of adding the MgCl_2 fragment to the $(\text{MgCl}_2)_3$ cluster

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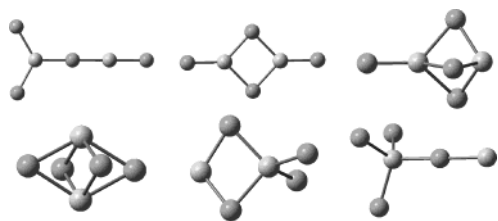


Figure 1. Initial structures of $(\text{MgCl}_2)_2$ isomers.

was to form a new four-membered cyclic substructure. With these limitations, the number of isomers was reduced from several thousand to 51, apparently without the loss of essential structures. The initial structures are presented in Figures 1–3. Only a minority of the initial structures turned out to be geometry minima. Table 1 gives the number of theoretical and optimized structures and the number of isomers that are geometry minima for each cluster size.

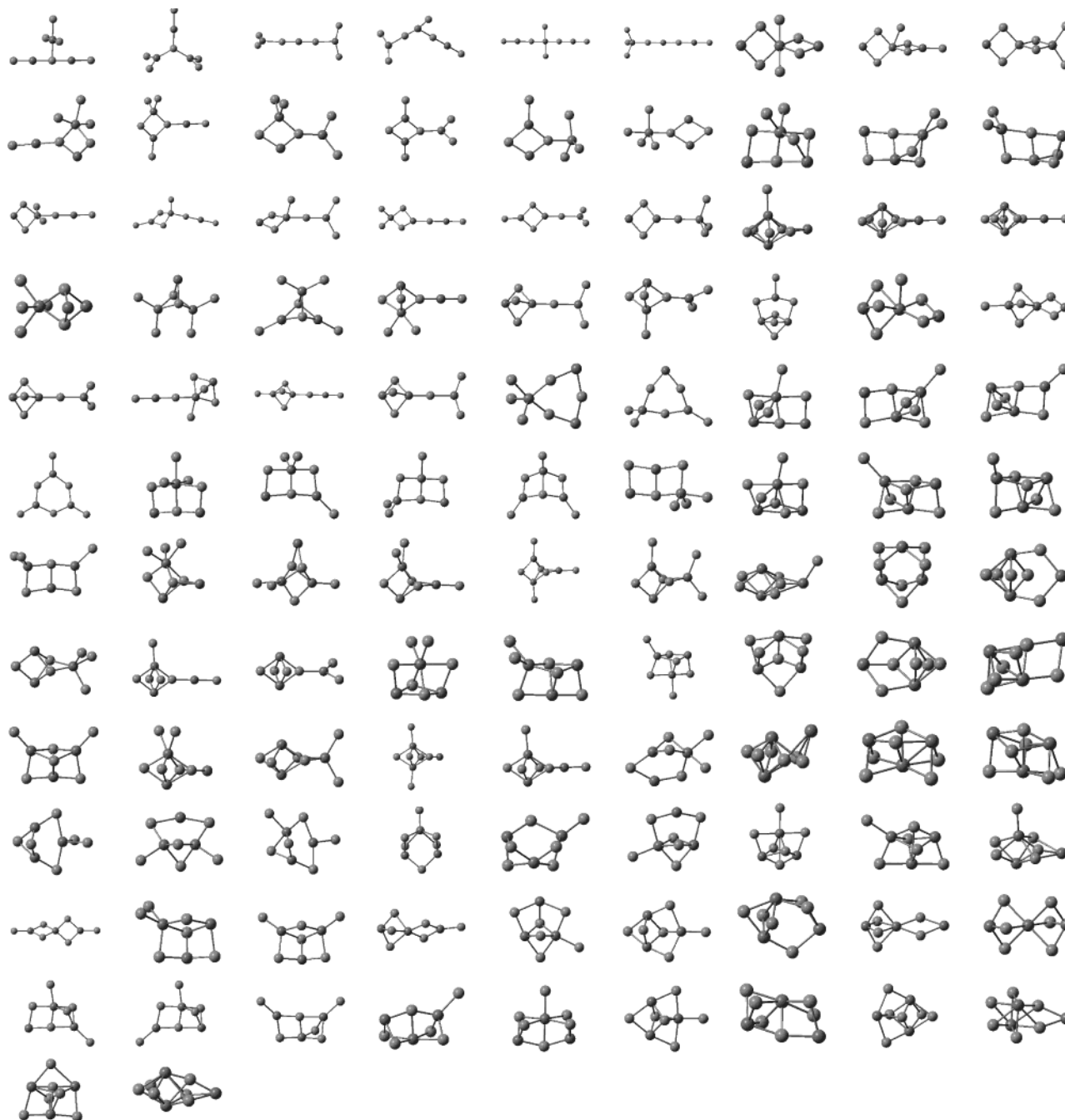
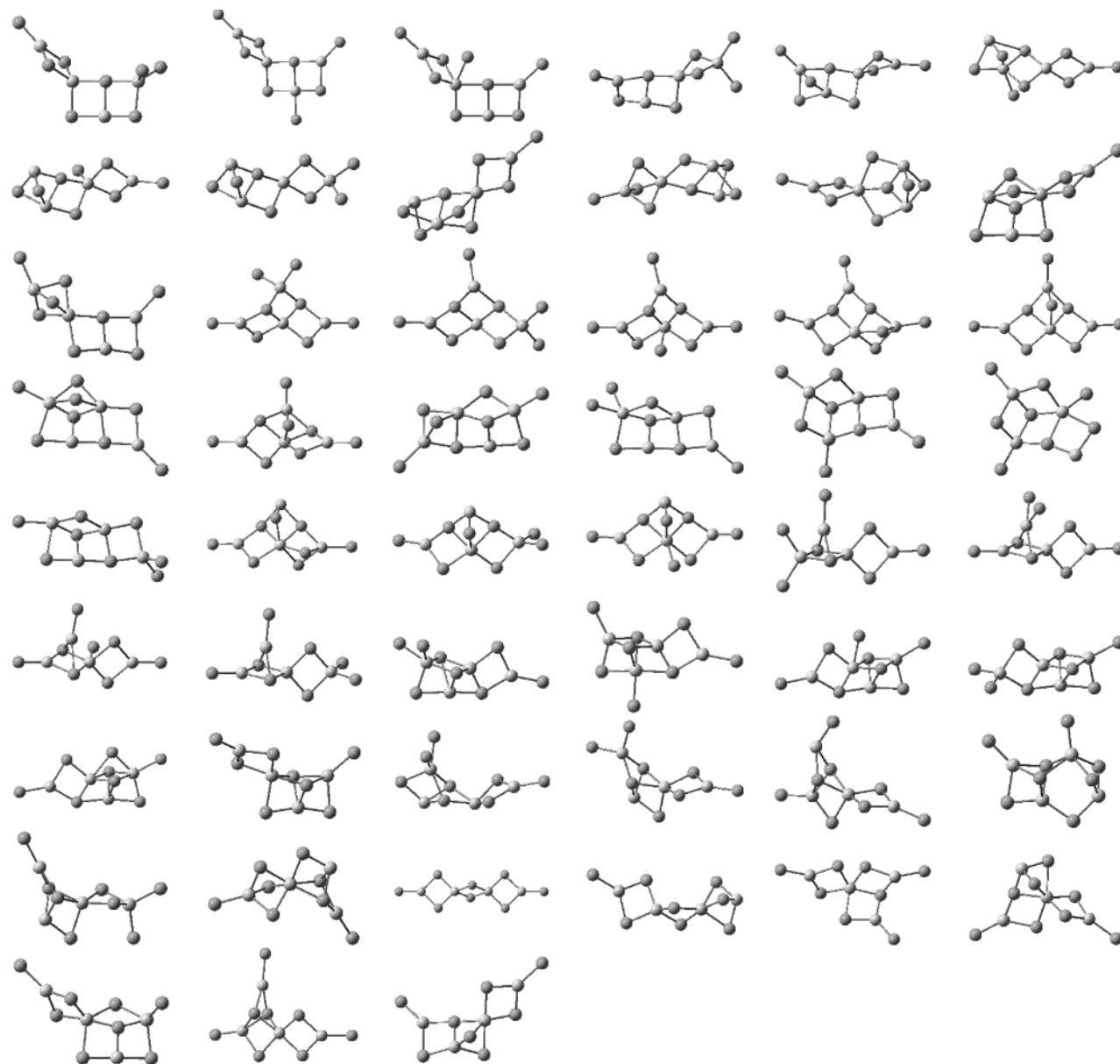



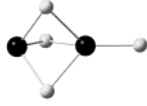
Figure 2. Initial structures of $(\text{MgCl}_2)_3$ isomers.

The initial structures were first screened with HF/3-21G* optimizations. The obtained geometry minima were reoptimized at the MP2/6-311G* level to verify the relevance of the HF/3-21G* structures and to obtain accurate relative stabilities for the isomers. All molecules were fully optimized without symmetry constraints. The geometry minima were confirmed by frequency calculations. The ab initio calculations were carried out with the Gaussian 98 program package.¹³

Results and Discussion

Isomers of $(\text{MgCl}_2)_2$. The MgCl_2 monomer is linear,^{5–10} and at the MP2/6-311G* level, the $\text{Mg}–\text{Cl}$ bond lengths are 2.181 Å, which is within the experimental range of 2.179 ± 0.005 Å.⁹ Dimerization of MgCl_2 to $(\text{MgCl}_2)_2$ increases the number of theoretical isomers to six (Table 1). Each possible isomer was optimized, and the initial structures are shown in Figure 1. The structures and relative stabilities of the isomers of $(\text{MgCl}_2)_2$

Figure 3. Initial structures of $(\text{MgCl}_2)_4$ isomers.**TABLE 2: Structures and Relative Stabilities of $(\text{MgCl}_2)_2$ Clusters and Number of Atoms with the Specified Coordination Number^a**

Complex	$\Delta E_{\text{HF/3-21G}^*}$ (kJ/mol)	$\Delta E_{\text{MP2/6-311G}^*}$ (kJ/mol)	$n_c(\text{Mg})$	$n_c(\text{Cl})$
	0.0	0.0	2(3)	2(2) 2(1)
2.1				
	50.1	57.4	1(4) 1(3)	3(2) 1(1)
2.2				

^a Bold.

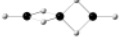


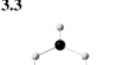
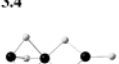



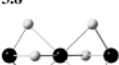

and the number of atoms with the specified coordination number are presented in Table 2. Of the six theoretical isomers, two turned out to be geometry minima.

The $(\text{MgCl}_2)_2$ dimer has been studied by experimental techniques.^{5,9,10} Structural parameters are available from a combined electron diffraction and computational study by Molnár et al.⁹ The preferred isomer (**2.1**) is a planar D_{2h} -

symmetric four-membered ring with two bridging ($n_c = 2$) and two terminal ($n_c = 1$) chlorines, which are bonded to 3-coordinated magnesium. At the MP2/6-311G* level, the $\text{Mg}-\text{Cl}_{\text{terminal}}$ bond length is 2.182 Å, and the $\text{Mg}-\text{Cl}_{\text{bridging}}$ bond distances are elongated to 2.353 Å owing to higher coordination. Experimental values are 2.188 ± 0.007 and 2.362 ± 0.010 Å, respectively. The structure is also in agreement with earlier theoretical studies.^{11,12,14–16} The less-stable isomer is C_{3v} -symmetric **2.2**, where magnesium atoms are connected via three chlorine bridges, leaving just one terminal chlorine. The coordination numbers of Mg are 3 and 4. This C_{3v} -symmetric isomer has also been found in earlier studies.^{11,12,14} The geometries and relative stabilities generated by the HF/3-21G* method are in good agreement with the results of the much more expensive MP2/6-311G* calculations.

Isomers of $(\text{MgCl}_2)_3$. All theoretical $(\text{MgCl}_2)_3$ trimers were studied, excluding those with unfavorable 1-coordinated magnesium atoms. This exclusion reduced the number of isomers to be studied from 139 to 110. Initial structures of these 110 isomers are presented in Figure 2. Despite the wide variety of initial geometries, only 10 structures turned out to be geometry

TABLE 3: Structures and Relative Stabilities of (MgCl₂)₃ Clusters and Number of Atoms with the Specified Coordination Number^a

Complex	$\Delta E_{\text{HF/3-21G}^*}$ (kJ/mol)	$\Delta E_{\text{MP2/6-311G}^*}$ (kJ/mol)	n_{Mg}	n_{Cl}
	0.0	0.0	1(4)	4(2)
3.1			2(3)	2(1)
	14.6	22.4	3(4)	2(3)
3.2			2(2)	2(1)
	68.5	72.9	1(4)	1(3)
3.3			2(3)	2(2)
	78.7	94.0	3(3)	3(2)
3.4			3(1)	3(1)
	82.0	76.9	1(5)	5(2)
3.5			2(3)	1(1)
	91.3	99.3	2(4)	5(2)
3.6			1(3)	1(1)
	94.2	transforms to 3.2	3(4)	1(3)
3.7			4(2)	1(1)
	140.3	150.0	2(4)	4(2)
3.8			1(2)	2(1)
	151.4	145.5	1(6)	6(2)
3.9			2(3)	
	202.6	200.3	3(4)	6(2)
3.10				

^a Bold.

minima after the HF/3-21G* screening. A large number of the initial guesses were transformed to the same minima during the optimization process. In subsequent MP2/6-311G* optimizations, one higher-energy structure (**3.7**) was transformed to a more stable isomer (**3.2**), and the number of isomers was reduced to 9. Table 3 presents the structure of the (MgCl₂)₃ clusters together with relative stabilities and the number of atoms with the specified coordination number.

The most stable Mg₃Cl₆ isomer is *D*_{2d}-symmetric **3.1**, which is formed from two perpendicularly oriented four-membered rings connected via a 4-coordinated Mg atom. The Mg–Cl bond lengths are very similar to those of the most stable dimer (**2.1**), namely, 2.183 Å for Mg–Cl_{terminal} and 2.355 Å for Mg–Cl_{bridging} at the MP2/6-311G* level, and they are also in good agreement with earlier calculations.^{11,12} Eichkorn et al.¹² studied six isomers of Mg₃Cl₆, but our systematic procedure produced 10 geometry minima for Mg₃Cl₆. The three lowest-energy isomers, **3.1** (*D*_{2d}), **3.2** (*C*_{2v}), and **3.3** (*C*_s), as well as less stable isomers **3.9** (*D*_{3d}) and **3.10** (*D*_{3h}), were also found by Eichkorn et al.¹² Their sixth isomer was a *C*_s-symmetric fragment of the lattice, which was also one of our initial structures. During the optimization process, however, this *C*_s-symmetric structure was transformed

to a more stable *C*_{2v}-symmetric isomer (**3.2**). We remind the reader that we did not incorporate any symmetry constraints into the calculations.

As noted above, various structures are conceivable for Mg₃Cl₆ trimers. An especially interesting structure, which has not been reported earlier, is the fifth most stable isomer **3.4**. Similar planar *D*_{3h}-symmetric trimers are preferred in some alkali halides, such as Li₃F₃ and K₃Cl₃,¹⁷ as well as in cuprous chloride (Cu₃Cl₃).¹⁸ Other metal halides have been reported in a comprehensive review article by Hargittai.¹⁹ A very similar structure is also preferred by 3-coordinated aluminoxanes.²⁰ In magnesium dichlorides, this isomer is approximately 90 kJ/mol less stable than the preferred isomer **3.1**.











The wide variety of isomers that were found now allows us to establish certain stability rules. First, coordination numbers of less than 3 for magnesium (**3.8**) are strongly disfavored. In the absence of other destabilizing structural characteristics or distortions, coordination numbers of 3 for magnesium are favored whenever the adoption of planar orientation is achievable (**3.1**, **3.3**, **3.4**). Likewise, in the absence of destabilizing characteristics or distortions, structures with tetrahedral 4-coordinated magnesium atoms are preferred (**3.1**–**3.3**). Mg₃Cl₆ trimers are still too small for conclusions to be drawn about the stabilities of isomers with coordination numbers higher than 4 (**3.5**, **3.9**). Chlorines may be present with coordination numbers of 1–3.

The geometries and relative stabilities produced by the HF/3-21G* method are generally in good agreement with the results of MP2/6-311G* calculations. The stabilities of the three most stable isomers are predicted with good accuracy, but the stability of the six-membered ring structure (**3.4**) is somewhat overestimated compared to the MP2/6-311G* result. In addition, the stability order of **3.8** and **3.9** is reversed by the higher-level method.

Isomers of (MgCl₂)₄. The number of isomers increases rapidly when the size of the magnesium chloride cluster is increased. As many as several thousand theoretical isomers are conceivable for Mg₄Cl₈. Because systematic investigation of thousands of isomers is not practical or even necessary, further approximations were required. As shown above, certain structural characteristics are preferred, including coordination numbers of 3 or more for magnesium, a planar orientation of 3-coordinated magnesium, and a tetrahedral arrangement of 4-coordinated magnesium. Hence, we proceeded by selecting the most stable Mg₃Cl₆ isomer (**3.1**) as the basic unit, and to this a new MgCl₂ fragment was added in all possible ways. Structures with 2-coordinated magnesium atoms were omitted. The remaining 51 initial structures of (MgCl₂)₄ clusters are shown in Figure 3. The resulting geometry minima, 10 at the HF/3-21G* level and 8 at the MP2/6-311G* level, together with the relative stabilities and the number of atoms with the specified coordination number, are presented in Table 4.

Calculations on the two most stable isomers, *C*_{2h}-symmetric **4.1** and *D*_{2h}-symmetric **4.2**, have been reported by Eichkorn et al.¹² Our systematic procedure produced those and several more geometry minima. Although many possible isomers of Mg₄Cl₈ do not appear in Table 4 owing to the applied approximations, most of the relevant structures are apparently presented. The preferred structural characteristics discussed above for the isomers of Mg₃Cl₆ are evident here as well; planar 3-coordinated and tetrahedral 4-coordinated magnesium atoms are favored. In addition, the contribution of higher coordination numbers of magnesium is now more significant. The stability difference between the preferred structure and the 5-coordinated isomer

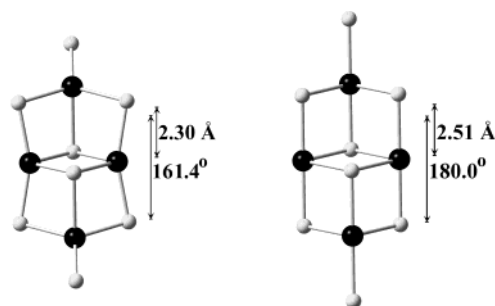
TABLE 4: Structures and Relative Stabilities of $(\text{MgCl}_2)_4$ Clusters and Number of Atoms with the Specified Coordination Number^a

Complex	$\Delta E_{\text{HF/3-21G}^*}$ (kJ/mol)	$\Delta E_{\text{MP2/6-311G}^*}$ (kJ/mol)	$n_i(\text{Mg})$	$n_i(\text{Cl})$
	0.0	0.0	4(4)	2(3) 4(2) 2(1)
4.1				
	20.3	13.5	2(4) 2(3)	6(2) 2(1)
4.2				
	52.9	57.4	4(4)	2(3) 4(2) 2(1)
4.3				
	58.4	49.1	1(5) 2(4) 1(3)	2(3) 4(2) 2(1)
4.4				
	68.2	69.8	4(4)	1(3) 6(2) 1(1)
4.5				
	73.1	transforms to 4.1	2(4) 2(3)	1(3) 4(2) 3(1)
4.6				
	81.3	83.3	1(5) 2(4) 1(3)	3(3) 2(2) 3(1)
4.7				
	82.1	78.4	3(4) 1(3)	2(3) 3(2) 3(1)
4.8				
	83.5	transforms to 4.2	3(4) 1(3)	1(3) 5(2) 2(1)
4.9				
	114.0	121.9	1(5) 2(4) 1(3)	2(3) 4(2) 2(1)
4.10				

^a Bold.

is about 80 kJ/mol for Mg_3Cl_6 , whereas the energy difference has decreased down to 50 kJ/mol for Mg_4Cl_8 (isomer **4.4**). The qualitative accuracy of the HF/3-21G* method is good; the stabilities of **4.3** and **4.7** are only a little overestimated relative to the MP2/6-311G* calculations.

It is actually no surprise that the C_{2h} -symmetric **4.1** is the most stable Mg_4Cl_8 isomer. This species represents a small fragment of the magnesium dichloride lattice.³ The similarities between isomer **4.1** and the fragment of the lattice are clear (Figure 4). The few differences are due to the effect of the surrounding atoms on the structure of the fragment of lattice. Two major deviations can be seen (Figure 4). First, the straight Cl—Mg—Cl angle of the lattice is distorted to 161.4° in isomer **4.1**. The origin of this distortion becomes apparent in a consideration of the coordination numbers of magnesium.

**Figure 4.** Structures of isomer **4.1** and the fragment of the lattice.³
















Whenever possible, the 4-coordinated magnesium of isomer **4.1** adopts the preferable tetrahedral orientation. In contrast to this, the corresponding 4-coordinated magnesium atom of the lattice fragment is actually 6-coordinated if the surroundings of the fragment are taken into consideration. The magnesium atoms of the lattice therefore prefer square-bipyramidal geometry, which is the favored orientation for 6-coordinated atoms. The second clear difference between isomer **4.1** and the lattice fragment appears in the Mg—Cl bond lengths. The distance between magnesium and the 2-coordinated chlorine is considerably shortened, from 2.506 Å in the lattice to 2.304 Å in cluster **4.1**. Because the magnesium atoms of the lattice are 6-coordinated, they form longer Mg—Cl bonds than the 4-coordinated magnesium atoms of the cluster.

Higher Oligomers of $(\text{MgCl}_2)_n$. Higher oligomers of magnesium dichloride were derived up to $n = 9$. On the basis of the building rules of the preferred Mg_4Cl_8 tetramer and simple chemical intuition, three low-energy isomers were constructed for the pentamer, hexamer, heptamer, octamer, and nonamer. The selected structures, together with the relative stabilities and the number of atoms with the specified coordination number, are presented in Table 5. Because the accuracy of the Hartree—Fock method is close to that of MP2, HF/3-21G* results are reported for higher oligomers beyond the tetramer.










The pentamer of magnesium dichloride has only one relevant isomer (**5.1**), representing the fragment of lattice. The other two presented isomers (**5.2** and **5.3**) are somewhat artificial and lie much higher in energy, 47.3 and 58.3 kJ/mol, respectively. Switching to the hexamer increases the number isomers so that three clusters resembling the fragment of lattice can be constructed. In this context, the first reasonable structure containing a 6-coordinated magnesium atom is introduced (**6.2**). This structure is, however, not preferred but is 14.2 kJ/mol less stable than isomer **6.1**, having two 5-coordinated and four 4-coordinated magnesium atoms. The low-energy structures of the heptamer show the significance of terminal chlorines. Isomers **7.1** and **7.2**, containing the minimum number of two terminal chlorines, are clearly favored over isomer **7.3** with four terminal chlorines. The same applies for the octamer as well, isomer **8.1**, with the minimum number of terminal chlorines being favored. The nonamer is the smallest oligomer in which a 6-coordinated magnesium atom is present in the preferred isomer (**9.1**).

Relative Stabilities of $(\text{MgCl}_2)_n$. Relative stabilities of the preferred $(\text{MgCl}_2)_n$ clusters are summarized in Table 6. The stabilities increase systematically as a function of the size of the cluster, independently of the calculation method. This trend can be rationalized by considering the coordination numbers of magnesium. For the MgCl_2 monomer (**1.1**), an unstable 2-coordinated magnesium is required, clearly resulting in the lowest relative stability. The dimer (**2.1**) can adopt a structure where 3-coordinated magnesium atoms are arranged in a

TABLE 5: Structures and Relative Stabilities of (MgCl₂)_n Clusters (*n* = 5–9) and the Number of Atoms with the Specified Coordination Number^a

Complex	<i>n</i>	ΔE _{HF/3-21G*} (kJ/mol)	n ₁ (Mg)	n ₁ (Cl)
	5	0.0	4(4)	3(3)
5.1			1(5)	5(2)
				2(1)
	5	47.3	1(3)	2(3)
5.2			4(4)	5(2)
				3(1)
	5	58.3	1(5)	2(3)
5.3			3(4)	6(2)
			1(3)	2(1)
	6	0.0	2(5)	4(3)
6.1			4(4)	6(2)
				2(1)
	6	14.2	1(6)	4(3)
6.2			5(4)	6(2)
				2(1)
	6	18.6	1(5)	4(3)
6.3			5(4)	5(2)
				3(1)
	7	0.0	3(5)	5(3)
7.1			4(4)	7(2)
				2(1)
	7	4.1	1(6)	5(3)
7.2			1(5)	7(2)
			5(4)	2(1)
	7	99.2	1(6)	6(3)
7.3			6(4)	4(2)
				4(1)
	8	0.0	4(5)	6(3)
8.1			4(4)	8(2)
				2(1)
	8	37.4	1(6)	7(3)
8.2			2(5)	6(2)
			5(4)	3(1)
	8	50.2	1(6)	7(3)
8.3			2(5)	6(2)
			5(4)	3(1)
	9	0.0	1(6)	8(3)
9.1			4(5)	8(2)
			4(4)	2(1)
	9	18.9	5(5)	7(3)
9.2			4(4)	9(2)
				2(1)
	9	53.6	2(6)	8(3)
9.3			2(5)	8(2)
			5(4)	2(1)

^a Bold.**TABLE 6: Relative Stabilities of the Preferred (MgCl₂)_n Clusters**

Complex	<i>n</i>	E _r /n (a.u.)		ΔE _r (kJ/mol)	
		HF/3-21G*	MP2/6-311G*	HF/3-21G*	MP2/6-311G*
	1	-1113.472723	-1119.088134	148.1	138.2
1.1					
	2	-1113.507825	-1119.1207408	55.9	52.5
2.1					
	3	-1113.520831	-1119.133212	21.8	19.7
3.1					
	4	-1113.529110	-1119.140729	0.0	0.0
4.1					
	5	-1113.533339	-1119.145256	-11.1	-11.9
5.1					
	6	-1113.537153	-1119.149371	-21.1	-22.7
6.1					
	7	-1113.539280	-1119.151705	-26.7	-28.8
7.1					
	8	-1113.540947	-1119.153553	-31.1	-33.7
8.1					
	9	-1113.542932	-1119.156225	-36.3	-40.7
9.1					

favorable planar orientation. The stability increases further upon moving to the trimer (**3.1**), in which tetrahedral 4-coordinated magnesium appears for the first time. Five-coordinated magnesium is introduced by the pentamer (**5.1**) in the orientation of a trigonal bipyramid. To reach the preferred coordination number of 6 for magnesium while maintaining the minimum number of terminal chlorines, we need to increase the size of the cluster up to the nonamer (**9.1**). Consequently, larger cluster are produced by repetitions of the Mg₄Cl₈ tetramer, which can hence be considered to be the basic unit although not itself containing 6-coordinated square-bipyramidal magnesium atoms. It follows that the convergence to the bulk structure can be already seen in the structure of the Mg₄Cl₈ tetramer.

It should be noted that relative stability order of magnesium dichloride oligomers was determined by total-energy calculations alone. Entropy effects are significant, explaining why MgCl₂ vapor consists mostly of monomers and dimers (i.e., of the least-

favoring oligomers on the basis of total energy). This is due to a greater number of energy levels in the vapor phase compared to the number in liquid and solid states, thus increasing the entropy of the system owing to the dispersal of energy. Another issue that needs to be considered is the basis set superposition error (BSSE). To check this effect, we calculated BSSE-corrected energies for oligomers up to tetramers. The BSSE corrections systematically increased the stability of the super-system, therefore not affecting the stability order of magnesium dichloride oligomers.

Conclusions

The structural characteristics of small $(\text{MgCl}_2)_n$ clusters, where $n = 1-4$, were systematically studied by ab initio Hartree–Fock and MP2 methods on a search for an interlink between magnesium dichloride clusters and lattices. A systematic technique was developed to handle in a reasonable manner the large number of theoretical isomers. The application of this technique and the rejection of structures of lesser significance left 168 magnesium dichlorides to be optimized. The resulting geometry minima were analyzed to draw conclusions on the structural preferences of $(\text{MgCl}_2)_n$ clusters. Higher oligomers, up to nonamers, were derived from the building principles of the preferred tetramer.

The performance of HF/3-21G* was very good: the results were mostly in agreement with those of the much more expensive MP2/6-311G* calculations. For oligomers up to tetramers, coordination numbers of 3 or more are favored for magnesium. The major structural characteristics of the most stable isomers are planar 3-coordinated and tetrahedral 4-coordinated magnesium centers. The preferred Mg_4Cl_8 cluster (**4.1**), possessing solely 4-coordinated tetrahedral magnesium atoms, already shows clear similarities to a fragment of the MgCl_2 lattice. Higher oligomers are produced by the repetition of this basic unit, converging toward the crystal structure of the MgCl_2 lattice. This result is useful in the understanding of the formation of magnesium dichloride bulk structure. The developed methodology should be adaptable to the study of other ionic compounds as well.

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Supporting Information Available: Systematic construction of the isomers of magnesium dichloride clusters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

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