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Molecular Structures of Magnesium Dichloride Sheets and Nanoballs

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The structures and relative stabilities of $(MgCl_2)_n$ sheetlike clusters and nanoballs were studied by quantum chemical methods. The sheets as discrete molecules were studied up to $Mg_{100}Cl_{200}$. Their stabilities increase systematically as a function of the size of the sheet. Periodic ab initio calculations were performed for (001) monolayer sheets of α- and β-$MgCl_2$, β-sheet being slightly favored. Nanoballs were constructed from Archimedean polyhedra, producing tetrahedral, octahedral, and icosahedral symmetries, and were studied up to $Mg_{60}Cl_{120}$. Nanoballs prefer to take the shape of truncated cuboctahedron ($Mg_{48}Cl_{96}$). Comparisons to sheetlike clusters and periodic calculations suggest that magnesium dichloride nanoballs are stable.

Introduction

Magnesium dichloride is a common inorganic compound, which has important practical applications. It has a significant industrial role as a support in olefin polymerization catalysis.[1] The solid-state structure is known to exist in three different crystalline forms: rhombohedral α-structure,[2] hexagonal close-packed β-form,[3] and δ-lattice,[4]which is a rotationally disordered version of β-form. The β-lattice is a layered system consisting of individual $MgCl_2$ sheets with an interlayer distance of 5.9 Å. The shortest distance between the layers is the Cl−Cl separation of 3.8 Å.[3] Spherical $MgCl_2$ supports have been recently synthesized and applied in Ziegler−Natta olefin polymerization catalysis.[5] The molecular structure of the spherical support is not known.

Notwithstanding the knowledge on solid state structures, experimental structural data on magnesium dichloride clusters are nearly nonexistent; structural parameters are available only for the monomer[6] ($MgCl_2$) and for the dimer[6,7] (Mg_2Cl_4). Theoretical studies on the structures of magnesium dichlorides have mainly focused on small clusters, up to tetramer (Mg_4Cl_8).[8] Eichkorn et al.[8d] have studied selected large clusters up to $Mg_{24}Cl_{48}$. Theoretical investigations suggest that the most stable clusters are generally sheetlike fragments of lattice, hence supporting the convergence of $(MgCl_2)_n$ clusters to the bulk structure of magnesium dichloride.[8d,8f]

In this work we explore planar and spherical structures for magnesium dichloride. Following the discovery of fullerenes[9] and carbon nanotubes,[10] it was discovered that nanostructured materials can be obtained also from inorganic compounds. Among many others, these include boron nitride fullerenes[11] and alumina nanotubes.[12] Furthermore, several nanoscale structures based on Platonic Solids and Archimedean polyhedra have been synthesized.[13] We report here the structures and stabilities of single-walled magnesium dichloride nanoballs derived from Archimedean polyhedra and compare them with sheetlike $MgCl_2$ clusters as well as with periodic ab initio calculations on $MgCl_2$ sheets.

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Computational Details

Periodic Hartree−Fock calculations were performed with CRYSTAL98[14] using default settings. Tightening the convergence criteria or increasing the number of ***k***-vectors has no practical influence.[15] The basis sets for both Mg and Cl were adopted from the work of Barrera et al.,[15] which are modifications of the basis sets of 8−5−11G* for Mg and 8−6-311G* for Cl developed for β-$MgCl_2$ by Harrison and Saunders.[16] We selected the best basis sets, basis set 3, of Barrera et al., with further optimized 3sp, 4sp, and 3d functions for Mg, and optimized 4sp, 5sp and 3d functions for Cl. Furthermore, 4d functions were added for Cl.[15]

Magnesium dichloride clusters and nanoballs were studied by Gaussian 03 quantum chemical software.[17] Calculations were performed by ab initio Hartree−Fock method using the basis sets modified by Barrera et al., here as well. The Hartree−Fock method was recently demonstrated to produce structures and stabilities for $(MgCl_2)_n$ clusters, which are in a good agreement with MP2 calculations.[8f] Molecules were constrained to the symmetry in question. Frequency calculations were performed for the nanoballs up to $Mg_{48}Cl_{96}$, to confirm the nature of the stationary points.

Results and Discussion

$(MgCl_2)_n$ Sheets. Several crystal structures have been determined for magnesium dichloride. For Periodic Hartee-Fock calculations, we selected two crystalline forms, α and β, characterized by Partin et al.[18] and Bassi et al.,[3] respectively. The unit cells were cut to form (001) monolayer sheets from the crystals. The results of the periodic calculations are presented in Table 1. The sheet cut from β form of magnesium dichloride is 2.3 kJ/mol per $MgCl_2$ more stable than the corresponding sheet of α form. This is in line with the calculated stabilities of α and β crystals, which are close to each other, β being slightly favored.[15]

Table 1. Total Energies of (001) Monolayer Sheets Cut from α and β Crystalline Forms of Magnesium Dichloride from Periodic Hartree−Fock Calculations

crystalline form	E_{sheet}/$MgCl_2$ unit (au)	ΔE_{sheet}/$MgCl_2$ unit (kJ/mol)
α[a]	−1118.820102	2.3
β[b]	−1118.820978	0.0

[a] Ref 17. [b] Ref 3.

Table 2. Relative Stabilities of Optimized Sheetlike $(MgCl_2)_n$ Clusters Systematically Constructed up to $i = j = 5$[a]

$i \times j$	formula	n	E/n (au)	$\Delta E/n$ (kJ/mol)
2 × 2	Mg_4Cl_8	4	−1118.795980	65.7
3 × 2	Mg_6Cl_{12}	6	−1118.802636	48.2
4 × 2	Mg_8Cl_{16}	8	−1118.805650	40.3
3 × 3	Mg_9Cl_{18}	9	−1118.806441	38.2
5 × 2	$Mg_{10}Cl_{20}$	10	−1118.807366	35.8
4 × 3	$Mg_{12}Cl_{24}$	12	−1118.809140	31.1
5 × 3	$Mg_{15}Cl_{30}$	15	−1118.810697	27.0
4 × 4	$Mg_{16}Cl_{32}$	16	−1118.811330	25.5
5 × 4	$Mg_{20}Cl_{40}$	20	−1118.812764	21.6
5 × 5	$Mg_{25}Cl_{50}$	25	−1118.814052	18.2

[a] The energy values are given relative to the β-$MgCl_2$ sheet.

Mg_4Cl_8 was chosen as the basic structural unit for the construction of magnesium dichloride sheetlike clusters. The cluster represents the smallest reasonable model for the fragment of lattice.[8f] All larger sheetlike clusters were built by extending the basic structure by repetitive $MgCl_2$ units in two dimensions of the plane (i,j). Combinations of i and j were studied systematically up to $i = j = 5$. Construction of the sheets is presented in Figure 1.

The relative stabilities of optimized sheetlike $(MgCl_2)_n$ clusters are shown in Table 2. The energy values are given relative to the periodic calculation of the (001) sheet cut from the β-lattice. Stabilities increase systematically as a function of the size of the cluster, independent of its shape, approaching the energy of a periodic β-sheet. It should be noted that direct comparison between the optimized sheets and the periodic calculation is not straightforward. An experimental Mg−Cl bond length of 2.51 Å, applied in periodic calculations, deviates somewhat from that of the optimized clusters, approaching 2.53 Å at the central part of the sheet. Consequently, the stability of the periodic β-sheet becomes slightly underestimated by the method applied. Destabilization of the periodic β-sheet is not significant, however, since the Mg−Cl distance predicted by the Hartree−Fock method is very close to the one characterized by experimental techniques. Therefore, periodic calculations can be employed as a reference when estimating the stabilities of optimized clusters.

The major structural difference between the monolayer sheet from crystal and the optimized sheetlike magnesium dichloride clusters is the optimization of edges in the latter. To study this effect, single-point calculations on various magnesium dichloride sheets were performed. Since the (001) sheet cut from the β-crystal was slightly favored over the α-form, as demonstrated above, the studied clusters were constructed from the β-lattice. C_{2h}-symmetric clusters, where $i = j$, were studied up to $i = j = 10$, for which molecular formula is $Mg_{100}Cl_{200}$. Furthermore, optimized clusters were

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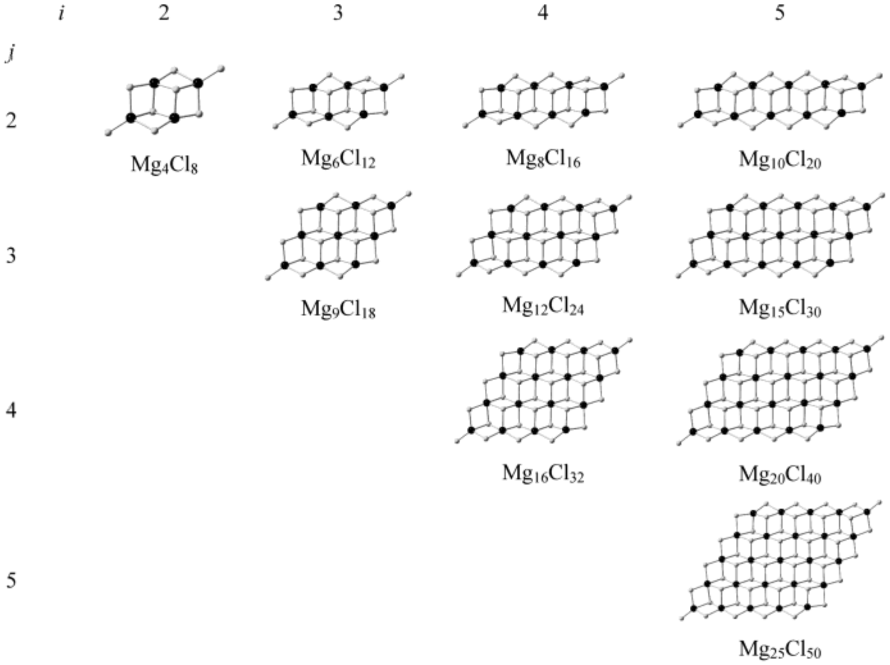

Figure 1. Systematic construction of sheetlike magnesium dichloride clusters from the Mg_4Cl_8 basic unit.

Table 3. Relative Stabilities and Ratios in the Number of Inner and Edge Mg Atoms ($[Mg_i]/[Mg_e]$) of Optimized (opt) and Frozen (sp) Sheetlike Magnesium Dichloride Clusters[a]

$i \times j$	formula	n	$[Mg_i]/[Mg_e]$	E_{opt}/n (au)	E_{sp}/n (au)	$\Delta E_{opt}/n$ (kJ/ mol)	$\Delta E_{sp}/n$ (kJ/ mol)
2 × 2	Mg_4Cl_8	4	0.00	−1118.795980	−1118.764991	65.7	147.1
3 × 3	Mg_9Cl_{18}	9	0.13	−1118.806441	−1118.786414	38.2	90.8
4 × 4	$Mg_{16}Cl_{32}$	16	0.33	−1118.811330	−1118.795189	25.3	67.8
5 × 5	$Mg_{25}Cl_{50}$	25	0.56	−1118.814052	−1118.802798	18.2	47.8
6 × 6	$Mg_{36}Cl_{72}$	36	0.80	−1118.815798	−1118.806714	13.6	37.5
7 × 7	$Mg_{49}Cl_{98}$	49	1.04	−1118.817014	−1118.808849	10.4	31.9
8 × 8	$Mg_{64}Cl_{128}$	64	1.29		−1118.810732		26.9
9 × 9	$Mg_{81}Cl_{162}$	81	1.53		−1118.812380		22.6
10 × 10	$Mg_{100}Cl_{200}$	100	1.78		−1118.813470		19.7
				−1118.822841[b]	−1118.823583[b]	−4.8	−6.8

[a] The energy values are given relative to β-$MgCl_2$ sheet. [b] Extrapolated to infinity by modified hyperbolic fit.

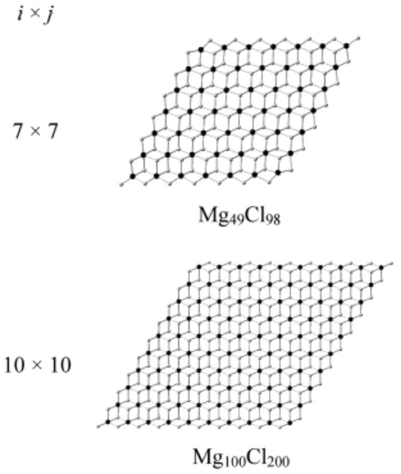

Figure 2. Largest optimized ($i = j = 7$) and frozen ($i = j = 10$) sheetlike $(MgCl_2)_n$ clusters.

extended up to $i = j = 7$, which is the first cluster containing more inner Mg atoms than edge Mg atoms. Largest optimized and frozen sheetlike clusters are illustrated in Figure 2. Stabilities relative to energy from periodic calculation of β-$MgCl_2$ sheet are given in Table 3.

The optimized sheetlike clusters are more stable than those of frozen, which is apparent and is due to the optimization of the edges. The effect is strongest for the Mg_4Cl_8 cluster, consisting of edge Mg atoms only. The difference in stability systematically decreases as a function of the cluster size, i.e., with increasing ratio in the number of inner and edge Mg atoms. For curiosity, we extrapolated the energies of both optimized and frozen clusters to infinity, to see if the influence of edge optimization vanishes. Both extrapolations lead to almost the same energy, −1118.8228 and −1118.8236 au for optimized and frozen sheets, respectively. It is also of interest to compare the extrapolated energies with the energy from periodic calculation of β-$MgCl_2$ sheet, which is −1118.8210 au. The energies are close to each other, extrapolations giving reliable, while somewhat higher stabilities.

$(MgCl_2)_n$ Nanoballs. Tetrahedral, octahedral, and icosahedral magnesium dichloride nanostructures were constructed from regular polyhedra. Generally, regular polyhedra can be classified into two families: platonic solids and Archimedean polyhedra. Platonic solids consist of regular convex polygon, whereas Archimedean polyhedra contain two or more different regular convex polygons, which are arranged so that every vertex is equivalent. All those polyhedra, in which five faces meet at each vertex, would produce 2:5 stoichiometry[19] and can thus be ruled out due to the requirement of 1:2 stoichiometry in magnesium dichlorides. Furthermore, the general preference of Mg_2Cl_2 rings in the compounds of magnesium dichloride considerably reduces the reasonable choices. While all those polyhedra, in which four faces meet at each vertex, would produce the correct stoichiometry, they would not contain any preferable Mg_2Cl_2 rings, and can hence be ruled out. Seven Archimedean polyhedra (truncated tetrahedron, truncated octahedron, truncated cube, truncated cuboctahedron, truncated icosahedron, truncated dodecahedron, and truncated icosidodecahedron) meet these criteria without losing the original symmetry.

The methodology for the construction of magnesium dichloride nanostructures is illustrated in Figure 3. The magnesium atoms are placed into the vertexes of each polyhedra, and the vertexes are connected via chlorine bridges so that single and double bridges alternate. Consequently, the planes formed by the adjacent magnesium atoms, which are not bound to each other, represent the faces of Archimedean polyhedra. The coordination numbers of magnesium and chlorine are 4 and 2, respectively.

Magnesium dichloride nanoballs were optimized up to $Mg_{60}Cl_{120}$. The relative stabilities are presented in Table 4 and are compared to periodic calculation of (001) monolayer sheet from β-$MgCl_2$. This particular comparison was chosen, since the studied nanoballs are single-walled. Correspondingly, bulk structure of $MgCl_2$ should be applied as a reference, when filled or multiwalled nanostructures are investigated. The four-coordinated magnesium atoms in the nanoballs are arranged in the preferred tetrahedral orientation. A slight exception is the smallest nanostructure, truncated tetrahedron ($Mg_{12}Cl_{24}$), which is strained due to its small size and therefore clearly the least stable. This is best seen in Cl−Mg−Cl angles of 123.2° between Mg_2Cl_2 and Mg_3Cl_3 rings, which somewhat deviate from the optimal tetrahedral angle of approximately 109°. This strain is already absent in truncated octahedron ($Mg_{24}Cl_{48}$), for which the corresponding angle between Mg_2Cl_2 and Mg_4Cl_4 rings is 114.4°. The Mg−Cl bond distances generally vary between 2.36 and 2.38 Å, excluding the strained truncated tetrahedron ($Mg_{12}Cl_{24}$), for which the range is 2.33−2.44 Å. The shorter Mg−Cl distances in nanoballs compared to approximately 2.5 Å in sheets is due to lower coordination numbers of Mg and Cl atoms. In nanoballs, the coordination numbers of Mg and Cl are 4 and 2, respectively, whereas sheets consist of 6-coordinated Mg atoms and 3-coordinated Cl atoms. The stabilities are practically independent of shape and size of the structures, excluding the strained truncated tetrahedron ($Mg_{12}Cl_{24}$). Truncated cuboctahedron ($Mg_{48}Cl_{96}$), consisting of Mg_2Cl_2, Mg_4Cl_4, Mg_6Cl_6, and Mg_8Cl_8 rings, is slightly favored.

The high stability of magnesium dichloride nanoballs is notable. Even the strained truncated tetrahedron ($Mg_{12}Cl_{24}$) is more stable than the sheetlike cluster of the same size (see Table 2). The same applies for larger nanoballs as well, which are favored over their sheetlike congeners. Furthermore, comparison to periodic calculation of monolayer sheet from β-lattice suggests that the nanoballs are stable. The energy difference between the monolayer sheet and the

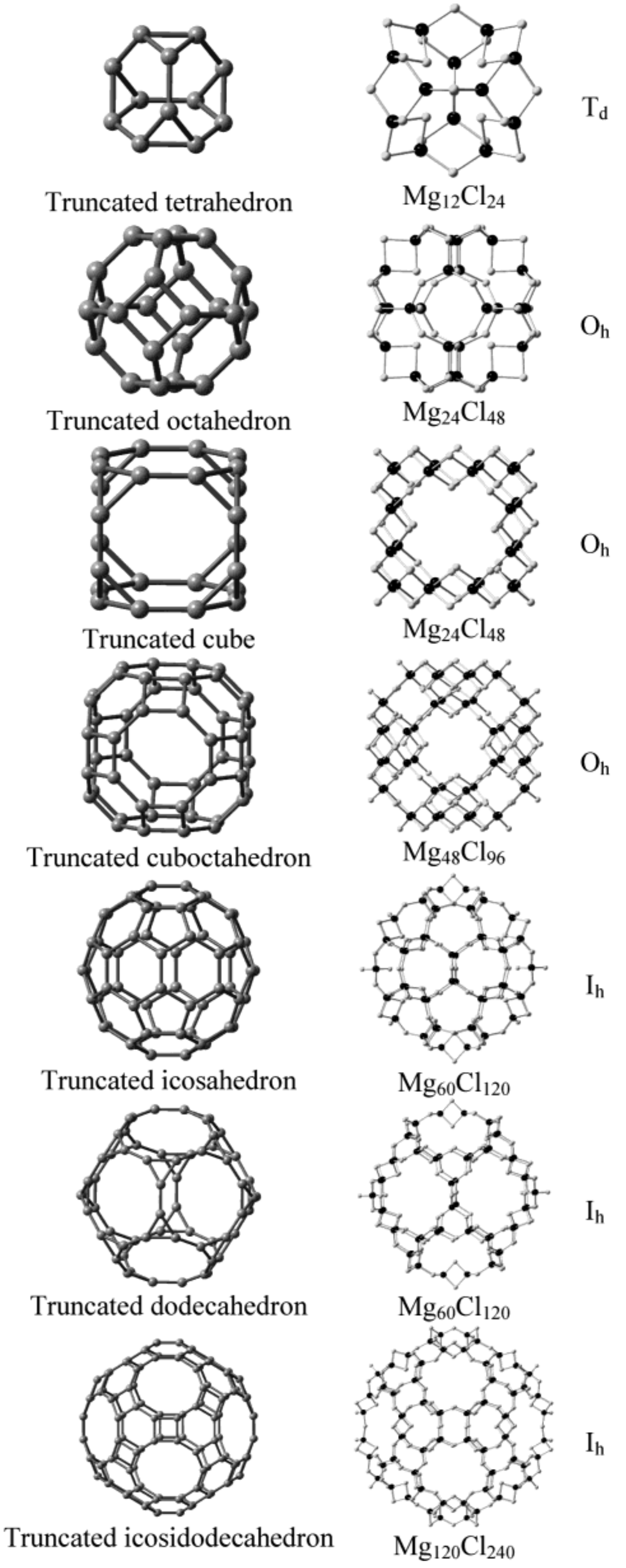

Figure 3. The structures and symmetries of magnesium dichloride nanoballs derived from Archimedean polyhedra.

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Table 4. Stabilities of Magnesium Dichloride Nanoballs Relative to Energy from Periodic Calculation of Monolayer Sheet of β-$MgCl_2$

parent polyhedra	formula	rings	n	E/n (au)	$\Delta E/n$ (kJ/mol)
truncated tetrahedron	$Mg_{12}Cl_{24}$	6 × Mg_2Cl_2 4 × Mg_3Cl_3 4 × Mg_6Cl_6	12	−1118.80991 1	29.1
truncated octahedron	$Mg_{24}Cl_{48}$	12 × Mg_2Cl_2 6 × Mg_4Cl_4 8 × Mg_6Cl_6	24	−1118.81718 5	10.0
truncated cube	$Mg_{24}Cl_{48}$	12 × Mg_2Cl_2 8 × Mg_3Cl_3 6 × Mg_8Cl_8	24	−1118.81720 5	9.9
truncated cuboctahedron	$Mg_{48}Cl_{96}$	24 × Mg_2Cl_2 12 × Mg_4Cl_4 8 × Mg_6Cl_6 6 × Mg_8Cl_8	48	−1118.81771 4	8.6
truncated icosahedron	$Mg_{60}Cl_{120}$	30 × Mg_2Cl_2 12 × Mg_5Cl_5 20 × Mg_6Cl_6	60	−1118.81667 1	11.3
truncated dodecahedron	$Mg_{60}Cl_{120}$	30 × Mg_2Cl_2 20 × Mg_3Cl_3 12 × $Mg_{10}Cl_{10}$	60	−1118.81761 3	8.8

favored nanoball, truncated cuboctahedron ($Mg_{48}Cl_{96}$), is only 8.6 kJ/mol/*n*, despite the lower coordination numbers in the nanostructure. Consequently, magnesium dichloride may have a tendency to form various nanostructures, of which the presented nanoballs serve just as examples. Magnesium dichloride nanotubes can be plausible, as well, if one considers the formation of carbon nanotubes from fullerenes. The layered bulk structure of $MgCl_2$ suggests that the nanostructures may be multiwalled.

Conclusions

The structures and relative stabilities of magnesium dichloride sheetlike clusters and nanoballs were determined by ab initio Hartree−Fock method. The sheets, which represent a fragment of the $MgCl_2$ lattice, were optimized up to $Mg_{49}Cl_{98}$. Furthermore, single-point calculations for (001) sheets of β-$MgCl_2$ lattice were performed up to $Mg_{100}Cl_{200}$. The nanoballs were built from tetrahedral, octahedral, and icosahedral Archimedean polyhedra by placing magnesium atoms into the vertexes. The magnesium atoms were connected via chlorine bridges to meet the requirement of 1:2 stoichiometry. Nanoballs up to $Mg_{60}Cl_{120}$ were optimized. The stabilities of both sheetlike clusters and nanoballs were estimated by comparisons to periodic Hartree−Fock calculations on monolayer sheets from crystal lattice.

The relative stabilities of $MgCl_2$ sheets systematically improve as a function of the size of the sheet, approaching the energy from periodic calculation of β-$MgCl_2$ sheet, which is slightly favored over the α-form. Extrapolation of both optimized and frozen sheets to infinity yielded practically the same energy, which is due to disappearance of edge effects. The stabilities of extrapolated sheets are in a good agreement with periodic calculation of the energy of β-$MgCl_2$ sheet. The $MgCl_2$ nanoballs prefer to take the shape of truncated cuboctahedron ($Mg_{48}Cl_{96}$), while being relatively insensitive to shape and size of the structures. Interestingly, the relative stabilities of nanoballs are higher than those of corresponding sheetlike clusters, earlier considered as the favored $MgCl_2$ clusters, and are close to the energy of β-$MgCl_2$ sheet obtained from periodic calculation. This suggests that magnesium dichloride may have a tendency to form nanostructures.

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Supporting Information Available: Listings of input and output Cartesian coordinates, input keywords and basis sets. This material is available free of charge via the Internet at http://pubs.acs.org.

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