Unusual Dimer Structures of the Heavier Alkaline Earth Dihalides: A Density Functional Study

Jack B. Levy[†] **and Magdolna Hargittai***[,‡]

Department of Chemistry, University of North Carolina at Wilmington, Wilmington, North Carolina 28403, and Structural Chemistry Research Group of the Hungarian Academy of Sciences, Eötvös University, Pf. 32, H-1518 Budapest, Hungary

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Density functional theory has been applied to investigate the monomeric and dimeric dihalides of the heavier alkaline earth metals. Quasirelativistic pseudopotentials and large basis sets with uncontracted d (and f) polarization functions on the metals and correlation-consistent all-electron basis sets on the halogens were utilized. The monomers of SrF_2, BaF_2, and $BaCl_2$ were found to be genuinely bent, while CaF_2 and $SrCl_2$, although also bent, have extremely flat potential energy surfaces and are better described as quasilinear. The dimers of the heavier alkaline earth difluorides and dichlorides, Ca_2F_4, Ca_2Cl_4, Sr_2F_4, Sr_2Cl_4, Ba_2F_4, and Ba_2Cl_4, were investigated in great detail. Six different isomers were calculated for the strontium and barium dihalide dimers. The typical D_{2h} symmetry halogen-bridged structure is the most stable only for the dimers of the lighter dihalides, and it is not a stable structure for the heavier dimers. For these molecules, a triple-bridged C_{3v} symmetry structure is the most stable and even other isomers with pyramidal coordination of the metal were found to be stable, although with higher energy. There appears to be a correlation between the monomer and the dimer structures for alkaline earth dihalides; for the linear halides, the metal tends to have planar, while for the bent ones, pyramidal coordination in their most stable dimer structure. Not only have our calculations extended information on this class of compounds but they have also considerably improved the agreement between the calculated and the available experimental data.

Introduction

The molecular shapes of alkaline earth dihalides are remarkably diverse. This diversity has generated a continued interest in and some controversy about these structures. The halides of the heavier alkaline earth metals have recently become accessible to computational studies, and a pattern of these structures is finally emerging.

The early notions of uniform linearity for all alkaline earth dihalides appeared consistent with popular qualitative models[1,2] as well as the rudimentary gas-phase electron diffraction studies in the fifties.[3] To be sure, the linear geometries reported from the early electron diffraction studies carried error limits up to ±30° or more, but they could be conveniently overlooked. For some time, however, there has been accumulating evidence that some of them, viz., strontium difluoride and all the barium dihalides are bent rather than linear.[4] Some molecules, such as calcium difluoride, strontium dichloride, and strontium dibromide are conspicuously floppy, and can be considered "quasilinear".[5−7] It is somewhat arbitrary what is considered quasilinear, a molecule that has a very slight hump on the potential energy surface at the linear geometry or one whose PES is simply extremely flat. These shapes cannot be predicted by such popular and successful models of structural chemistry as the VSEPR model[1] and the simple Walsh-type diagrams.[2]

The first indication of the possible nonlinearity of alkaline earth dihalide molecules came from Klemperer's molecular beam deflection studies in the early sixties.[8] They were later supported by electron diffraction studies,[9] and finally confirmed by recent computations.[5,10,11] Other nonlinear geometries in molecules of heavy alkaline earth metals with two coordination have also been observed, by X-ray diffraction[12] and electron diffraction[13] experiments and computations.[14] Both core polarization in the metal and d orbital participation in the bonding can be invoked to account for this "anomalous" structural behavior.

In view of the diversity in the monomer structures of the two-coordinated alkaline earth metals, it is also of interest to look at the structure of their dimers. There have been a few studies discussing these structures for the alkaline earth dihydrides,[15] and for the lighter dihalides.[16−19] The levels of the computations and the depth of these studies differ considerably.

Kaupp and Schleyer[15] probed several different isomers in their study of the dihydrides and suggested some interesting structures for the dimers of the heavier metals. Ystenes and Westberg only considered the usual D_{2h} geometry in their study of the magnesium dihalide dimers.[18] Ramondo et al. tested three different isomers of the beryllium and magnesium difluorides.[16] Axten et al.[17] and Pogrebnaya et al.[19] looked at several different models of the magnesium dihalides, and the beryllium, magnesium, and calcium difluorides, respectively. The models that were considered are summarized in Figure 1 but the general conclusion pointed to the D_{2h} structure (**1**) for the dimers of the dihalides (except for CaF_2, vide infra). Alas, the dimers of heavier dihalides have not been studied, while the "anomalous" monomers have proved to be those of the heavier metals. Thus, our curiosity together with the computational possibilities motivated us to initiate the present investigation into the dimer structures of the heavier alkaline earth dihalides.

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* To whom correspondence should be addressed. E-mail: hargittaim@ludens.elte.hu.

[†] University of North Carolina at Wilmington.

[‡] Eötvös University.

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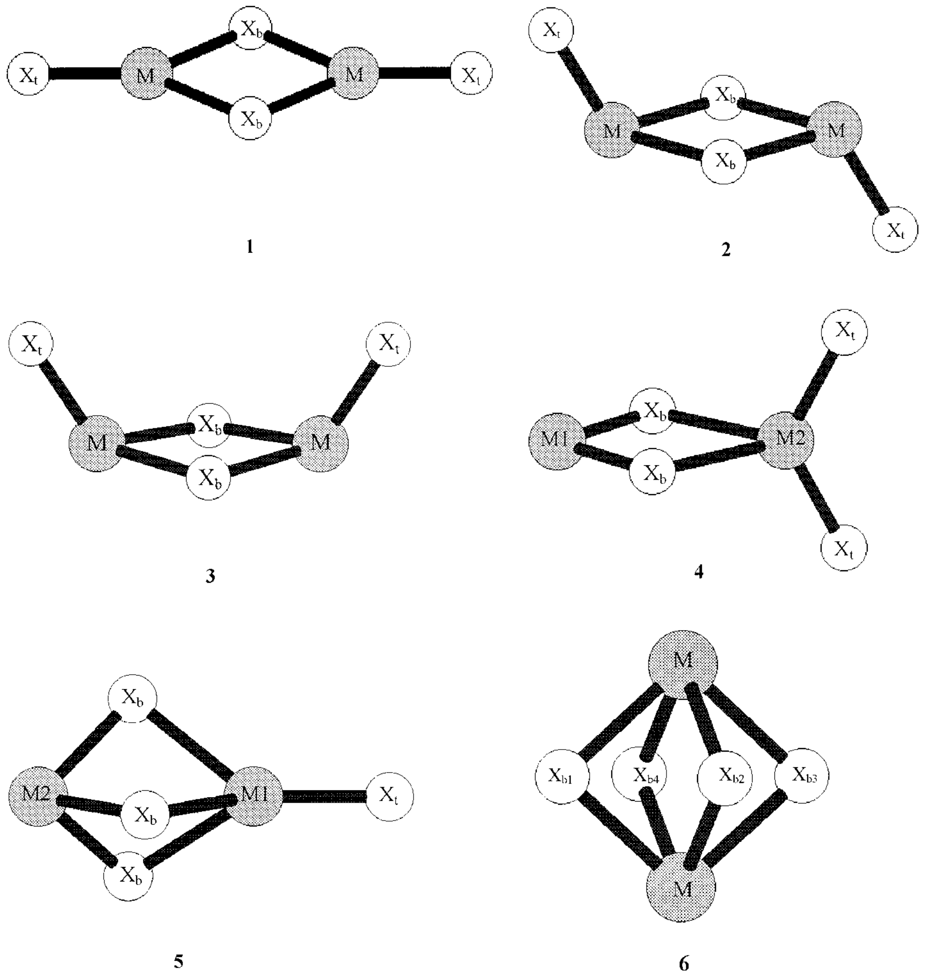

Figure 1. Different possible isomers of alkaline earth dihalides and dihydrides: **1**, D_{2h}, two halogen (or hydrogen) bridges; **2**, C_{2h}, two ligand bridges with pyramidal metal coordination and trans arrangement of the terminal atoms; **3**, C_{2v}, two ligand bridges with pyramidal metal coordination and cis arrangement of the terminal atoms; **4**, C_{2v}, with two ligand bridges and asymmetrical arrangement of the terminal atoms; **5**, C_{3v}, three ligand bridges; **6**, D_{4h}, four ligand bridges.

While the computations quoted above found the dimers of beryllium and magnesium dihalides and magnesium dihydrides to have the D_{2h} symmetry structure in their ground state, there was no consistency in the data concerning other possible isomers. According to Ramondo et al.,[16] both Be_2F_4 and Mg_2F_4 have a second stable minimum structure with C_{3v} symmetry (**5**) that is separated by a rather large energy gap from the global minimum (166.9 and 66.1 kJ/mol for Be_2F_4 and Mg_2F_4, respectively, at the HF/6-31G* level). Pogrebnaya et al.[19] did not find the C_{3v} structure stable for Be_2F_4, but their results agree with the previous one for Mg_2F_4, with a similar energy difference from structure **1** (64.5 kJ/mol at the HF and 58.0 kJ/mol at the MP2 level, respectively). Axten et al.[17] arrived at similar conclusions in their study of all magnesium dihalides. They found the C_{3v} symmetry structure stable and higher in energy than the D_{2h} structure by 66.1 and 64.0 kJ/mol for Mg_2F_4, at the HF and MP2 level, respectively. The energy differences are the same for all four Mg_2X_4 molecules at the HF level, but decrease somewhat toward the magnesium di-iodide dimer at the MP2 level, viz., 58.6, 52.3, and 35.6 kJ/mol, for Mg_2Cl_4, Mg_2Br_4, and Mg_2I_4, respectively. There were no other stable isomers found for either the beryllium or the magnesium dihalide dimers. Considering Mg_2H_4, only the D_{2h} structure was found to be stable. The triple-bridged structure (**5**) has two imaginary frequencies and is not even bound with respect to two monomer molecules.[15]

Calcium is the first among the alkaline earth metals for which a nonlinear monomer structure has been proposed in one of its dihalides; CaF_2 is calculated to be bent and extremely floppy (but see basis set and method dependence below),[20] while CaH_2 is calculated to be linear with a very shallow bending potential.[21] Considering their dimers, the ground-state structure of Ca_2H_4 is characterized by model **1** with D_{2h} symmetry, but two further structures, **5** and **6**, were also found to be stable. The C_{3v} symmetry structure (**5**) with three hydrogen bridges is only slightly less stable than the D_{2h} structure (**1**) with energy differences of 17.2 and 5.9 kJ/mol at the HF and MP2 levels, respectively. The structure with four hydrogen bridges (**6**) has considerably higher energy (159.4 and 130.5 kJ/mol at the HF and MP2 levels, respectively). For CaF_2, the global minimum is structure **5**, with three halogen bridges. The D_{2h} symmetry structure (**1**) is only slightly less stable (4.0 and 11.6 kJ/mol, at HF and MP2, respectively). Again, structure **6** was found to be a stable structure, but with considerably higher energy (142.8 kJ/mol at HF and 129.5 kJ/mol at MP2) than structure **5**.

In the present study, we determined the geometry of the dimers of strontium and barium difluoride and dichloride by quantum chemical calculations. Since all previous studies used either HF or MP2 level calculations, we repeated the calculations of Ca_2F_4 at these levels together with the B3LYP technique applied here, to check the performance of both the applied basis sets and the density functional method. Similarly, we have calculated the structure of Ca_2Cl_4, so that we could compare our geometries with experimental structures. To be able to do meaningful comparisons with the structure of the monomers, we have calculated the structure of the six corresponding monomer structures as well, with the same computational techniques.

Computational Methods

Calculations were performed using the Gaussian 98 program package.[22] For the alkaline earth metals, the multielectron adjusted quasirelativistic 10-valence-electron effective core potentials (WB MEFIT) and 6s6p5d1f uncontracted basis sets developed by the Stuttgart group were used.[21] These pseudopotentials treat the major relativistic effects, such as the Darwin and mass velocity terms, but do not include spin−orbit interaction. It is obvious that the use of d polarization functions is essential for the description of these molecules. Moreover, it has been pointed out that even the contraction scheme of the d orbitals is important in determining the shape of these molecules, so uncontracted d polarization functions have to be used.[10] For fluorine and chlorine all-electron basis sets, the correlation-consistent basis sets of Dunning,[23] cc-pVTZ, were used as implemented in Gaussian98.

The density functional method (B3LYP)[24] was selected as the principal computational method since it has proved to be reliable for calculating both the geometries and the vibrational characteristics of molecules containing heavy metals.[25] Full geometry optimizations were carried out within the point group of the particular structures. All stationary points were characterized by a frequency analysis at the same level as the optimizations. Since our first results indicated problems with the frequency analyses (too many imaginary frequencies together with considerable nonzero translational contributions remaining), we repeated our initial calculations with an ultrafine grid with 99 radial shells and 590 angular points. This step proved to be crucial since the problems with the frequency analyses disappeared and the CPU times were about the same and sometimes even shorter due to faster convergence. It is important to mention though that only the energies, the convergence, and the very low wavenumbers were sensitive to the change in the grid size but not the geometrical parameters. Compared with the other geometries, structure **6** is a relatively rigid system, and therefore for this model the default fine grid calculation proved to be sufficient.

Since these are the first DFT calculations that have been performed on systems under investigation in the present study, we found it prudent to repeat the computations for Ca_2F_4 at the HF and MP2 level together with the same DFT approach used for the other molecules. The structure of Ca_2Cl_4 was calculated in order to compare it with available experimental data. These calculations were performed only for the typical D_{2h} structure and the triple-bridged C_{3v} symmetry structure.

Results

Monomers. The monomer geometries were calculated at the same level and with the same basis sets as the dimers so that geometrical changes during dimerization could be reliably observed. Moreover, since there are prior computational data available for the monomers at the HF and MP2 level, the applicability of the DFT method could also be tested. For this reason CaF_2 and $CaCl_2$ were also calculated; CaF_2 because that is the best studied system computationally (vide infra) and $CaCl_2$, because for this molecule there is reliable experimental information for the monomer and even a limited amount of information for the dimer.[26] The monomer geometries, together with previous results both from experiment and computation, are collected in Table 1.

Experimental data are scarce to compare the computational results with, mostly because these halides have such a low volatility. The few data that are available are also often of questionable value. A case in point is the old Russian electron diffraction works,[3] which were pioneering in their time but do not conform to present-day standards. These data are still often quoted but any agreement or disagreement with them no longer carries information value (for a critical discussion, see ref 4 and especially ref 33). The few more up-to-date electron diffraction data are quoted in Table 1. Concerning bond angles, there are some estimates from matrix isolation vibrational spectroscopic studies,[27,29−32] but they are rather uncertain, considering the shortcomings of the matrix isotope shift technique in determining bond angles.[20a,34] Furthermore, the bond angle estimates from matrix isolation techniques are impacted by matrix effects, which can be considerable for highly flexible molecules with soft bending modes. Examples amply illustrate this in the literature; even the symmetry of the molecule can change from one matrix to another and to the gas phase.[30,35] An early high-temperature gas-phase infrared spectroscopic study[36] yielded merely some rough indication about the bond angles of these molecules.

Calcium Dihalides. The experimental difficulties in determining the molecular geometries of these alkaline earth dihalides enhance the importance of the computational approaches. However, due to the very shallow bending potential of some of these molecules, the determination of their shape is a delicate task that has been amply demonstrated by the large number of computational studies and their scattered results on the structure of CaF_2 (see the examples given in Table 1 and references to other studies in the cited works). It appears that both the bond length and the shape of the molecule depend strongly on the applied basis sets as well as the method of the computation. According to the careful study of Hassett and Marsden,[20a] a large number of polarization functions is needed to describe CaF_2, and the result is very sensitive even to the applied exponents. It was also shown that the HF level is not sufficient to describe this molecule properly, so correlated levels must be used. Wright et al.[20b] also demonstrated the basis set dependency of these structures.

Our MP2 results for both the bond length and the bond angle of CaF_2 are in excellent agreement with other, high-level all-electron calculations (see Table 1), thus giving confidence about our chosen pseudopotentials and basis sets. As to the B3LYP results, both the bond length and the bond angle seem somewhat underestimated by this method, as compared with the MP2 results. There is no good-quality experimental bond length for CaF_2 to compare with nor reliable enough bond angles from experiments (vide supra); but considering the most recent bond angle estimate from spectroscopy,[27] from among all computations our B3LYP result agrees with it best.

The linearity of $CaCl_2$ is well established by spectroscopic[28,31] and electron diffraction[26] experiments as well as by computations.[5,10] Before comparing its computed bond length with the one from gas-phase electron diffraction, vibrational anharmonic corrections of the thermal average experimental bond lengths have to be carried out, due to the different physical meaning of the experimental and computed parameters.[37,38] The estimated experimental equilibrium bond length for $CaCl_2$ is 2.455(8) Å. Among the computed Ca−Cl bond lengths our B3LYP result agrees best with this value, so the reliability of the applied method and basis set seems to be established.

TABLE 1: Geometrical Parameters of the Monomers (Distances in Å, Angles in Degrees) from Experiment (in Italics) and Computation

r(M−X)	∠X−M−X	method[a]	distance type/basis set[b] M	distance type/basis set[b] X	ref
CaF_2					
	142(1)	*MI(Ar)-IR*			*27, 28*
	140	*MI(Kr)-IR*			*29*
	139−156[c]	*MI-IR*			*30*
2.017	163.0	HF	pp/uc	ae	this work
2.004	153.5	MP2	pp/uc	ae	this work
1.990	142.4	B3LYP	pp/uc	ae	this work
2.032	162.9	HF	ae/uc+f[d]	ae[d]	20a
2.003	153.8	MP2	ae/uc+f[d]	ae[d]	20a
2.005	153	MP2	ae/c+f	ae	20b,c
2.001	151.8	MP2	ae/uc+f	ae	20c
2.033	154.8	MP2	ae/uc	ae	20d
2.030	156.0	CISC	ae/uc	ae	20d
1.96	130	HF	ae/uc	ae/uc	20e
2.031	163	HF	ae/c	ae	19
2.037	180	HF	pp/c	pp+d	10
2.029	162.3	HF	pp/uc	pp+d	10
2.010	157.5	SDCI	pp/uc+f	pp+d	10
2.053	180	HF	pp/c	pp+d	5
$CaCl_2$					
2.483(7)	*180*	*ED*	r_g		*26*
2.455(8)		*ED*	r_e		*calc by us*
2.466	180	B3LYP	pp/uc	ae	this work
2.507	180	HF	pp/c	pp+d	10
2.506	180	HF	pp/uc	pp+d	10
2.482	180	SDCI	pp/uc+f	pp+d	10
2.540	180	HF	pp/c	pp+d	5
SrF_2					
	108	*MI(Kr)-IR*			*29*
2.120	129.0	B3LYP	pp/uc	ae	this work
2.167	143.3	HF	pp/c	pp+d	10
2.164	141.5	HF	pp/uc	pp+d	10
2.161	138.8	SDCI	pp/uc+f	pp+d	10
2.191	144	HF	pp/c	pp+d	5
2.177	149.0	HF	pp/c	pp+d	11
$SrCl_2$					
2.630(6)	*154.6(1.0)*	*ED*	$r_g/\angle_a$		6
2.613(8)		*ED*	r_e		6
	120	*MI(Kr)-IR*			*31*
	130(8)	*MI(Ar)-IR*			*32*
2.629	160.0	B3LYP	pp/uc	ae	this work
2.632	155.5	B3LYP	pp/uc+f	ae	6
2.621	160.6	MP2	pp/uc+f	ae	6
2.631	161.4	QCISD(T)	pp/uc+f	ae	6
2.612	155.2	QCISD(T)	pp/uc+2f	ae	6
2.678	180.0	HF	pp/c	pp+d	10
2.675	167.3	HF	pp/uc	pp+d	10
2.640	159.5	SDCI	pp/uc+f	pp+d	10
2.700	180	HF	pp/c	pp+d	5
2.689	180.0	HF	pp/c	pp+d	11
BaF_2					
	100	*MI(Kr)-IR*			*29*
2.236	117.8	B3LYP	pp/uc	ae	this work
2.300	125.3	HF	pp/c	pp+d	10
2.299	125.6	HF	pp/uc	pp+d	10
2.254	123.0	SDCI	pp/uc+f	pp+d	10
2.331	126	HF	pp/c	pp+d	5
2.291	126.0	HF	pp/c	pp+d	11
$BaCl_2$					
	100	*MI(Kr)-IR*			*31*
	120(10)	*MI(Ar)-IR*			*32*
2.764	128.4	B3LYP	pp/uc	ae	this work
2.846	144.9	HF	pp/c	pp+d	10
2.841	141.5	HF	pp/uc	pp+d	10
2.791	141.4	SDCI	pp/uc+f	pp+d	10
2.898	143	HF	pp/c	pp+d	5
2.816	143.1	HF	pp/c	pp+d	11

[a] Abbreviations (in alphabetical order): B3LYP, density functional calculation with Becke's three-parameter hybrid method with the LYP functional; CISC, size-consistent configuration interaction; ED, electron diffraction; HF, Hartree−Fock calculation; MI-IR, matrix isolation infrared spectroscopy; MP2, Moller−Plesset calculation; QCISD(T), quadratic configuration interaction including singe and double substitutions with a triples contribution; SDCI, singles and doubles configuration interaction. [b] Abreviations used for basis sets: ae, all electron; pp, pseudopotential (quasirelativistic or relativistic) or model potential method; c, contracted; uc, uncontracted d polarization functions; for further details see original references. [c] Depending on the applied matrix, see original reference for details. [d] Exponents of different d and f polarization functions optimized.

Strontium and Barium Dihalides. All four monomers studied (SrF_2, $SrCl_2$, BaF_2, and $BaCl_2$) appear bent in our B3LYP calculations using quasirelativistic core potentials and uncontracted d polarization functions on the metal. There is a general consensus about the bent shape of the two fluorides and of $BaCl_2$, as shown in Table 1, even if the actual values of the bond angle vary from technique to technique and from measurement to measurement. The case of $SrCl_2$ is ambiguous. Similar to CaF_2, the earlier studies, using contracted d functions, resulted in linear geometry for this molecule as did the use of simple HF level of computation.[5,10] A more recent study using only HF computations communicated also a linear geometry for this molecule.[11]

The preliminary results of our high-temperature electron diffraction investigation of $SrCl_2$ indicate a bent geometry, as do computations in which electron correlation is taken into account and in which uncontracted d basis functions are used.[6] Our present results agree with ref 6 concerning the bent shape and the bond angle of the molecule as well as the bond length.

Our monomer bond lengths seem to be much shorter than any of the previously published values, and these new data are consistent with the experimental equilibrium distances derived from the electron diffraction thermal-average parameters applying corrections for both harmonic and anharmonic vibrations. This observation is valid for both cases where experimental information is available. Our bond angles are also considerably smaller than the previously published computed ones, while they agree better with the available experimental values.

Table 2 lists the frequencies of all monomers studied here (from among the previous computations only the ones with reliable geometries are cited; that is, the studies using inadequate basis sets and therefore resulting in wrong molecular shapes are excluded). Experimental information is scarce and includes gas-phase as well as matrix isolation results. The most interesting feature of these data is the difficulty of reliably determining bending frequencies for the floppiest molecules, called also quasilinear, viz. CaF_2 and $SrCl_2$. The MI-IR studies of CaF_2 exaggerate the value of the bending frequency, and this may be an indication of some interaction with the matrix molecules. This is also suggested by the differing bond angles determined in different matrixes (see Table 1). For $SrCl_2$, the computed bending frequencies are extremely low and the bending potential of the molecule is extremely flat.[6] This makes these frequency values rather uncertain, but again, the MI-IR bending frequency can also be indicative of some matrix interaction that would increase its value.

There is a discrepancy in the frequency assignment for BaF_2, concerning the symmetric and antisymmetric stretching frequen-

TABLE 2: Vibrational Frequencies (cm^{-1}) and Their Symmetry Assignments of Monomeric Alkaline Earth Dihalides from Experiment (in Italics) and from Computations

method[a]	ν_1 (A_1/Σ_g)[b]	ν_2 (A_1/π_u)	ν_3 (B_2/Σ_u)	ref
CaF_2				
IR gas			*575(10)*	*36*
MI(Ar)-IR	*487.5*	*156.6*	*559.8*	*28*
MI(Kr)-IR	*486.2*	*163.6*	*553.5*	*28*
MI(Kr)-IR	*484.8*	*163.4*	*553.7*	*29*
IR[c]	*520(10)*		*595(10)*	*34*
B3LYP	524	88	598	this work
MP2	482	81	551	20d
CISC	479	90	549	20d
MP2	524	30	628	20c
HF	494	65	609	10
HF	506	53	631	19
$CaCl_2$				
IR gas			*395(7)*	*36*
MI(Ar)-IR		*71.5*	*397.2*	*28*
MI(Kr)-IR		*65.5*	*402.7*	*28*
MI(Kr)-IR		*63.6*	*402.3*	*31*
B3LYP	279	18	418	this work
HF	275	48	420	10
HF	265	50	442	5
SrF_2				
IR gas			*455(7)*	*36*
IR[c]	*485(10)*		*490(10)*	*34*
MI(Kr)-IR	*441.5*	*82.0*	*443.4*	*29*
B3LYP	480	91	482	this work
HF	465	77	480	10
HF	440	76	509	5
$SrCl_2$				
IR gas			*300(7)*	*36*
MI(Ar)-IR	*275*		*308*	*32*
MI(Kr)-IR	*269*	*44*	*300*	*31*
B3LYP	264	16	311	this work
MP2	279	24	330	6
B3LYP	266	28	311	6
HF	256	20	307	10
BaF_2				
IR gas			*415(7)*	*36*
IR[c]	*450(10)*		*430(10)*	*34*
MI(Kr)-IR	*389.6*		*413.2*	*29*
B3LYP	450	95	432	this work
HF	421	87	432	10
HF	406	77	436	5
$BaCl_2$				
IR gas			*265(5)*	*36*
MI(Ne)-IR	*262*	*62*	*268*	*32*
MI(Ar)-IR	*226*	*61*	*234/247*	*32*
MI(Kr)-IR	*255*		*260*	*31*
B3LYP	260	47	267	this work
HF	245	38	258	10
HF	233	36	275	5

[a] For meaning of abbreviations see Table 1. [b] Symmetry assignment corresponds to bent/linear geometries. [c] Corrected for matrix effects, based on measurements in different matrices.

cies. The two experimental studies[29,34] have an opposite assignment, while $\nu_3 < \nu_1$ in ref 34, $\nu_1 < \nu_3$ in ref 29. Curiously, there is also some disagreement in the computational results (see Table 2). According to our results, the IR intensity of the antisymmetric stretching frequency is about 3 times as high as that of the symmetric stretching frequency. Considering the published experimental spectra in refs 29 and 34, we tend to favor the assignment of Snelson, and suggest to accept $\nu_1 > \nu_3$. Our computed values of $\nu_1 = 450$ cm^{-1} and $\nu_3 = 432$ cm^{-1} almost coincide with the values estimated for the gas-phase by Snelson, based on his measurements in different matrixes. For all other molecules the agreement between experiment and different level computations is acceptable.

Dimers. *Calcium Difluoride and Calcium Dichloride Dimers.* The two calcium dihalides were studied in order to assess the reliability of our computational approach for these types of metal halides, and only structures **1** and **5** of Figure 1 were calculated. The geometrical parameters of these two dimers are given in Table 3 together with other data from the literature. Our HF results for Ca_2F_4 agree very well with those of ref 19, the only available comparison. Concerning Ca_2Cl_4, the difference of the terminal and bridging bonds, 0.21 Å, agrees well with the crude estimate from electron diffraction, 0.22(4) Å.[26]

Concerning the relative stability of these isomers, our results on Ca_2F_4 agree with the previous calculation by Pogrebnaya et al.,[19] at least at the HF level. Both structures were found to be stable minima, but the triple-bridged structure **5** is of somewhat lower energy than structure **1**. Pogrebnaya et al. found the energy difference to be 4.0 and 11.6 kJ/mol at the HF and MP2 levels, respectively. The energy differences in our calculations are 1.0, 6.4, and 7.9 kJ/mol at the HF, MP2, and B3LYP levels, respectively. There is, however, one interesting aspect of the B3LYP calculation; the D_{2h} isomer **1** is no longer a minimum structure but has one imaginary frequency, thus corresponding to a transition state. Since this structure was found to be a stable minimum at the HF level in ref 19, we also calculated the frequencies at the HF and the MP2 level and both resulted in all positive frequencies. In checking the performance of the DFT method further, we continued to increase the grid size from the 58 410 points, corresponding to the ultrafine grid, to 196 608 points (96 radial shells and a spherical grid), but it did not change the results. Thus, it appears that the DFT method may have problems with the frequency calculation for systems that have extremely flat potential energy surfaces. However, this does not influence the reliability of the geometrical parameters, as Table 3 illustrates this.

TABLE 3: Geometrical Parameters (Distances in Å, Angles in Degrees), Dipole Moments (in Debye), and Relative Energies (in kJ/mol) of Ca_2F_4 and Ca_2Cl_4

	Ca_2F_4				Ca_2Cl_4
	HF	HF (ref 19)	MP2	B3LYP	B3LYP
D_{2h} (**1**)					
$M-X_t$	2.011	2.027	2.000	1.990	2.450
$M-X_b$	2.195	2.203	2.186	2.185	2.660
X_b-M-X_b	75.9	75.7	77.3	77.9	87.0
C_{3v} (**5**)					
$M1-X_t$	2.027	2.042	2.015	2.002	2.462
$M1-X_b$	2.308	2.311	2.299	2.300	2.803
$M2-X_b$	2.101	2.114	2.088	2.082	2.558
X_t-M1-X_b	136.1	136.0	135.8	135.8	131.4
X_b-M2-X_b	82.6	82.2	83.4	83.7	81.0
μ	12.0	12.2	11.8	10.5	11.0
D_{2h}	1.0	4.0[a]	6.4	7.9	0
C_{3v}	0	0	0	0	2.5

[a] 11.6 kJ/mol for MP2 single-point calculation.

The dimer of $CaCl_2$ was found to have the usual D_{2h} symmetry global minimum structure (**1**), in accordance with earlier observations for other linear dihalide dimers[16−19] and with the interpretation of the FTIR spectrum of calcium dichloride.[28] Structure **5** is also a minimum, merely 2.5 kJ/mol higher in energy than structure **1**. Apparently, the Ca_2F_4 and

TABLE 4: Relative Stabilities of Different Isomers of Alkaline Earth Dihalide Dimers (in kJ/mol), the Number of Their Imaginary Frequencies, N_{imag}, and Dimerization Energies, ΔE, for the Most Stable Isomer (kJ/mol) from B3LYP Calculations

	Ca_2F_4		Ca_2Cl_4		Sr_2F_4		Sr_2Cl_4		Ba_2F_4		Ba_2Cl_4	
structures	energy	N_{imag}	energy	N_{imag}	energy	N_{imag}	energy	N_{imag}	energy	N_{imag}	energy	N_{imag}
D_{2h} (**1**)	7.9	1[a]	0	0	28.9	2	13.0	0	45.8	2	27.3	2[b]
C_{2h} (**2**)					21.9	0			19.7	0	22.0	0
C_{2v} (**3**)					25.7	0			27.5	0	25.3	0
C_{2v} (**4**)					152.9	1	125.9	1	139.7	1	120.9	1
C_{3v} (**5**)	0	0	2.5	0	0	0	0	0	0	0	0	0
D_{4h} (**6**)					103.7	0	110.4	0	64.9	0	78.8	0
ΔE (**5**)	−272.0				−279.1		−211.5		−247.1		−206.8	
ΔE (**1**)			−194.4									

[a] There are no imaginary frequencies at the HF level (see text). [b] Same at the HF level.

Ca_2Cl_4 pair is the point where the D_{2h} structure changes to the C_{3v} structure in the ground state, but in a subtle way, while the PES for both molecules remains extremely flat.

Strontium and Barium Dihalide Dimers. Relative Stabilities of Isomers. All possible structures indicated in Figure 1 were investigated since the main objective of this paper was the investigation of the heavy alkaline earth dihalides. Full geometry optimizations were carried out for all isomers, initially without any constraint and finally with only the point group symmetry restriction. All structures were found to be stationary points on the potential energy surface (except structures **2** and **3** for Sr_2Cl_4) but not all of them represent minima. The relative energies are given in Table 4. All molecules, except Sr_2Cl_4, show the same pattern. For all four molecules the C_{3v} symmetry structure **5** with three halogen bridges is the global minimum.

The generally accepted D_{2h} symmetry structure for metal dihalide dimers (**1**) is a true minimum only for Sr_2Cl_4, being only about 13 kJ/mol higher in energy than structure **5**. For the other three molecules **1** has two imaginary frequencies. Considering our findings for Ca_2F_4 regarding the stability of this structure, we also carried out a frequency calculation for the D_{2h} structure at the HF level, to see if the imaginary frequencies appear only with the DFT approach. However, the two imaginary frequencies remained; thus, it seems that this structure is, indeed, no longer a minimum for the heavier dimers. Its stability compared to **5** decreases about 100% in going from Sr to Ba with the same halogen and in going from Cl to F ligand for the same metal.

Isomers **2** and **3** with pyramidal configuration around the metal atom are true minima for all molecules except the strontium dichloride dimer, for which they refined to the D_{2h} symmetry geometry. For the other three molecules both **2** and **3** are a little lower in energy than the D_{2h} structure (**1**), with the structure with trans arrangement of the terminal halogens (**2**) being somewhat lower in energy than the cis arrangement (**3**).

Structure **6** with four halogen bridges and D_{4h} symmetry is a minimum structure for all four molecules, but these structures are rather high in energy compared to the ones discussed before. The energy difference compared to structure **5** is largest for Sr_2Cl_4, while it is the smallest for Ba_2F_4; the relative energies decrease considerably from Sr to Ba with the same halogen and also, although much less, from chlorine to fluorine with the same metal. This structure is different from all the others in that it is relatively rigid and therefore there was no reason to do the ultrafine grid calculations for it (vide supra).

Structure **4**, the one having C_{2v} symmetry and an unsymmetrical arrangement of the halogen ligands, is a transition structure for all four molecules with one imaginary frequency and rather large energy separation from the ground state structure **5**, the largest being 153 kJ/mol for Sr_2F_4 and the smallest 121 kJ/mol for Ba_2Cl_4.

TABLE 5: Geometrical Parameters (Distances in Å, Angles in Degrees) and Dipole Moments (in Debye) of the Ground-State, Triple-Halogen-Bridged Structure (5) of M_2X_4 Dimers

	Sr_2F_4	Sr_2Cl_4	Ba_2F_4	Ba_2Cl_4
$M1-X_t$	2.154	2.630	2.288	2.798
$M1-X_b$	2.451	2.959	2.626	3.137
$M2-X_b$	2.225	2.714	2.371	2.881
$M1\cdots M2$	3.262	3.631	3.585	3.994
X_t-M1-X_b	137.0	132.7	138.6	134.3
X_b-M2-X_b	81.1	87.9	78.7	84.9
μ	11.4	12.5	11.4	13.4

TABLE 6: Geometrical Parameters (Distances in Å, Angles in Degrees) of Dimers with Two Halogen Bridges[a]

	Sr_2F_4	Sr_2Cl_4[b]	Ba_2F_4	Ba_2Cl_4
		D_{2h} (**1**)		
$M-X_t$	2.139	2.614	2.270	2.779
$M-X_b$	2.341	2.829	2.510	3.015
$M\cdots M$	3.689	4.197	3.987	4.561
X_b-M-X_b	76.0	84.2	74.8	81.7
		C_{2h} (**2**)		
$M-X_t$	2.126		2.245	2.765
$M-X_b$	2.324		2.468	2.994
$M\cdots M$	3.676		3.972	4.544
X_b-M-X_b	75.5		72.8	81.3
$M-M-X_t$	139.3		113.3	137.4
		C_{2v} (**3**)		
$M-X_t$	2.131		2.244	2.769
$M-X_b$	2.333		2.479	3.003
$M\cdots M$	3.685		3.991	4.556
X_b-M-X_b	75.6		72.6	81.2
$M-M-X_t$	149.0		126.0	145.0
μ	6.9		10.4	9.0
		C_{2v} (**4**)		
$M1-X_b$	2.125	2.606	2.256	2.764
$M2-X_b$	2.571	3.094	2.795	3.299
$M2-X_t$	2.181	2.667	2.303	2.828
$M1\cdots M2$	3.670	4.139	4.030	4.549
X_t-M2-X_t	135.3	139.7	126.4	133.5
X_b-M2-X_b	68.9	77.9	65.3	74.2
X_b-M1-X_b	86.4	96.6	83.9	92.1
μ	17.9	19.0	19.2	21.3

[a] Dipole moments, when different from zero, are also given (in Debye). [b] Structures **2** and **3** are not stable minima for Sr_2Cl_4; they converge to structure **1**.

Geometries. The geometries of all isomers shown in Figure 1 were calculated for all four heavy metal dimers. The geometrical parameters are collected in Tables 5−7.

Isomer 5, C_{3v} Symmetry. For all four molecules, this structure is the global minimum. The variations of the geometrical parameters show similar trends (see Table 5). In all molecules, the terminal $M1-X_t$ bond is about 0.03 Å longer than the monomer bond (except for Sr_2Cl_4 for which the two are the same). The two different bridging bonds (bonds to different

TABLE 7: Geometrical Parameters (Distances in Å, Angles in Degrees) of the Four-Halogen-Bridged Isomers (6) of M_2X_4 Dimers

	Sr_2F_4	Sr_2Cl_4	Ba_2F_4	Ba_2Cl_4
$M-X_b$	2.346	2.869	2.489	3.025
$M\cdots M$	2.939	3.217	3.260	3.560
$X_{b1}-M-X_{b2}$	66.9	71.7	64.6	69.7
$X_{b1}-M-X_{b3}$	102.4	111.7	98.2	107.9
$M-X_b-M$	77.6	68.3	81.8	72.1

metal atoms) have strikingly different lengths; the bonds to the three-coordinated metal atom, $M2-X_b$, are only about 0.08 Å longer than the terminal bond, that is, much shorter than the usual bridging metal−halogen bonds. On the other hand, the bridging bonds connected to the four-coordinated metal atom, $M1-X_b$, are an additional 0.23−0.24 Å longer than the other bridging bond (that is they are 0.30−0.33 Å longer than the terminal bond), indicating a rather loose linkage. It may be best to characterize these molecules as $MX^+MX_3^-$ ion pairs.

Isomer 1, D_{2h} Symmetry. For the dimers of all linear metal dihalides and dihydrides, this structure is the global minimum.[15−19] However, as discussed above, this is not the case for the four molecules studied here. The geometrical parameters (Table 6) are more or less typical of this type of structure, the terminal metal halogen bonds being slightly longer (about 0.01−0.03 Å) than the corresponding monomer bond, except for the very floppy Sr_2Cl_4 and Ca_2F_4, for which the relationship is the reverse. For all molecules, the bridging bonds are consistently longer, by about 0.2 Å, than the terminal bonds. The X_b-M-X_b angles are smaller in the two fluorides than in the chlorides, in keeping with the smaller size of the bridging ligand. These structures, except for Sr_2Cl_4, are not minima on the potential energy surface.

Isomer 2, C_{2h} Symmetry. In this structure the two terminal halogen ligands occupy trans positions. For Sr_2Cl_4, this is not a stable structure as it converges to structure **1**. However, for the other three dimers this is the second deepest minimum on the potential energy surface, separated from the C_{3v} symmetry global minimum only by about 20 kJ/mol. Comparing their geometrical parameters (Table 6) with those of the monomer and the D_{2h} symmetry structure **1**, the terminal bonds are of about the same length as the monomer bonds for all four molecules, and both these and the bridging bonds are somewhat shorter than those in the D_{2h} structure of Sr_2F_4, Ba_2F_4, and Ba_2Cl_4. Considering the deviation from the D_{2h} symmetry structure, Ba_2F_4 is more pyramidal than Sr_2F_4 (the $Ba-Ba-F_t$ angle is about 26° smaller than the $Sr-Sr-F_t$ angle). Extrapolating this observation to the two dichlorides, it seems reasonable that this structure is not a stable one for Sr_2Cl_4, and, indeed, it converged to the D_{2h} structure.

Isomer 3, C_{2v} Symmetry. This structure differs from the previous one only in that the two terminal halogen ligands are in the cis rather than trans position with respect to each other. This structure is not stable for Sr_2Cl_4, and it is the third deepest minimum for the other three molecules, separated from structure **2** only by about 4−8 kJ/mol. The lengths of the terminal bonds (Table 6), are about the same as those of the monomer bonds, and the bridging ones are about 0.2−0.23 Å longer. Their ring geometry is the same as that of isomer **2**. Considering their deviation from the D_{2h} structure, the $M-M-X_t$ angles are about 10° larger than they are in **2**, which can be the result of the stronger anion−anion repulsion in a cis configuration.

Isomer 4, C_{2v} Symmetry. This is a highly unsymmetrical arrangement, and it represents a transition state for all four molecules (one imaginary frequency). This structure lies considerably, about 120−150 kJ/mol, higher in energy than structure **5**. The shortest bond in these molecules is the $M1-X_b$ bond, being about the same or slightly longer than the corresponding monomer bonds (Table 6). The $M2-X_t$ bond is about 0.05 Å longer than the $M1-X_b$ bond. At the same time, the other bridging bond, $M1-X_b$, is considerably longer than either of the others and is about 0.45−0.55 Å longer than the terminal bond. This shows that this isomer is a rather loosely bound complex of two MX_2 monomers.

TABLE 8: Vibrational Frequencies (cm^{-1}), Their Symmetry Assignments, and Infrared Intensities (km/mol) for Isomer 5 (C_{3v}) of the Dimers

	Ca_2F_4	Ca_2Cl_4	Sr_2F_4	Sr_2Cl_4	Ba_2F_4	Ba_2Cl_4
E	78 (8)	50 (2)	54 (13)	39 (4)	29 (14)	30 (5)
A_1	241 (2)	152 (0.1)	169 (1)	112 (1)	128 (0.4)	86 (1)
E	209 (59)	117 (18)	174 (50)	98 (20)	148 (39)	84 (18)
E	235 (8)	150 (11)	212 (5)	128 (5)	188 (4)	117 (3)
A_1	330 (113)	193 (54)	294 (132)	171 (6)	263 (147)	157 (70)
E	433 (154)	295 (107)	367 (106)	239 (69)	324 (99)	209 (62)
A_1	509 (170)	316 (92)	429 (106)	261 (46)	387 (138)	234 (43)
A_1	562 (160)	378 (125)	456 (131)	289 (9)	409 (120)	251 (92)

Isomer 6, D_{4h} Symmetry. This is an unusual structure with four halogen bridges connecting the two metal atoms and providing an unisotropic environment for the metals. However, even this structure is a true minimum for all four molecules, albeit with a very high energy (about 65−110 kJ/mol) relative to **5**. Considering its geometrical parameters (Table 7), the $M-X_b$ bonds are about 0.25 Å longer than the monomer bonds and about 0.02−0.033 Å longer than the bridging bonds in structures **2** and **3**. The metal−metal distances are much shorter, by about 0.75 Å in the fluorides and by 1.0 Å shorter in the chlorides, than in structures **1−3.** Compared to the similar dihydride dimers, their $M\cdots M$ distances are between those of the fluorides and the chlorides for both metals. The sum of the ionic radii of the metal dications (six coordination instead of four) is 2.64 and 2.98 Å for Sr^{2+} and Ba^{2+}, respectively, thus all $M\cdots M$ distances are longer than that. The comparison of the halogen$\cdots$halogen distances in the central plane of the molecule is especially of interest, considering halogen repulsions. The sum of the ionic radii for the fluorine and chlorine anions is 2.29 and 3.34 Å, respectively, so even these are within the $X\cdots X$ distances in these four isomers.

Vibrational Frequencies. Vibrational frequencies for all dimers were calculated. The D_{2h} structures (**1**) of Sr_2F_4, Ba_2F_4, and Ba_2Cl_4 have two imaginary frequencies, while the C_{2v} structure **6** for all four molecules has one imaginary frequency, indicative of the fact that these are not minima on the potential energy surface. All the other structures were found to be true minima. The vibrational frequencies of these species are given in Tables 8−12 together with their symmetry assignment and for the more stable ones with their infrared intensities, the latter in order to facilitate their assignment in experimental spectra. The frequencies of Ca_2F_4 and Ca_2Cl_4 for structures **1** and **5** are also included in the tables.

The heavier dimers have not been observed experimentally yet. Their lighter counterparts, such as Be_2X_4, Mg_2X_4, and even Ca_2X_4, have been observed by different techniques, such as mass spectrometry,[39] vibrational spectroscopy,[27,28,40] and electron diffraction.[26,41,42] Three wavenumbers of Ca_2F_4 have been identified and assigned in their matrix isolation spectra,[28] in agreement with our values (except for the assignment of one of the frequencies; see Table 9). Similarly, the two identified wavenumbers of the Ca_2Cl_4 spectrum[28] agree with the computed values. With further development of matrix isolation vibrational

TABLE 9: Vibrational Frequencies (cm^{-1}), Their Symmetry Assignments, and Infrared Intensities (km/mol) for Isomer 1 (D_{2h}) of the Dimers

		Ca_2F_4[a]		Ca_2Cl_4[b]	Sr_2F_4	Sr_2Cl_4	Ba_2F_4	Ba_2Cl_4
	B3LYP	MP2	HF (ref 19)	B3LYP	B3LYP	B3LYP	B3LYP	B3LYP
B_{2g}[c]	−27	23	13	35	−51	6	−63	−22
B_{3u}	8 (54)	21 (53)	21 (58)	18 (17)	−35 (62)	11 (22)	−54 (70)	−12 (28)
B_{2u}	64 (47)	68 (54)	68 (63)	40 (20)	48 (43)	33 (21)	31 (35)	28 (19)
B_{3g}	95	101	97	62	63	46	36	37
B_{3u}	159 (133)	168 (151)	175 (171)	95 (77)	120 (74)	70 (49)	91 (38)	55 (34)
A_g	183	189	194	108	131	82	97	65
B_{3g}	337	347	360	219	289	179	242	156
B_{2u}	381 (180)	379 (191)	382 (208)	272 (117)	314 (130)	212 (76)	277 (120)	183 (67)
A_g	383	385	396	231	334	206	292	183
B_{1u}	394 (129)	397 (103)	411 (91)	221 (39)	351 (221)	202 (67)	310 (316)	185 (110)
B_{1u}	559 (506)	556 (484)	581 (460)	377 (391)	460 (295)	293 (243)	416 (245)	255 (214)
A_g	587	582	604	397	477	303	429	264

[a] Experimental frequencies from matrix isolation infrared spectra: B_{1u}: 530 (Ar) and 527 (Kr); 368 (Ar) and 366 (Kr). B_{2u}: 396 (Ar) and 394 (Kr) from ref 28. [b] Experimental frequencies from matrix isolation infrared spectra: B_{1u}: 370 (Ar) and 386 (Kr); B_{2u}: 278 (Ar) and 269 (Kr) from ref 28. [c] Centrosymmetric normal modes are inactive in the infrared.

TABLE 10: Vibrational Frequencies (cm^{-1}) and Their Symmetry Assignments for Isomer 2 (C_{2h}) of the Dimers

	Sr_2F_4		Ba_2F_4		Ba_2Cl_4
B_u	30	B_u	18	B_u	14
A_g	45	A_g	50	A_g	25
A_u	59	A_u	54	A_u	32
B_g	87	B_g	88	B_g	47
B_u	138	A_g	116	B_u	66
A_g	143	B_u	129	A_g	72
B_g	295	B_g	260	B_g	159
A_u	310	A_u	270	A_u	181
A_g	341	A_g	303	A_g	187
B_u	364	B_u	336	B_u	193
B_u	470	B_u	434	B_u	260
A_g	480	A_g	436	A_g	265

TABLE 11: Vibrational Frequencies (cm^{-1}) and Their Symmetry Assignments for Isomer 3 (C_{2v}) of the Dimers

	Sr_2F_4	Ba_2F_4	Ba_2Cl_4
A_1	29	32	10
B_2	31	36	11
A_2	66	51	35
B_1	67	77	35
A_1	130	111	62
A_1	139	124	70
A_2	292	256	158
B_1	311	268	181
A_1	337	300	185
B_2	358	331	190
B_2	466	432	258
A_1	481	440	266

TABLE 12: Vibrational Frequencies (cm^{-1}) and Their Symmetry Assignments for Isomer 6 (D_{4h}) of the Dimers

	Sr_2F_4	Sr_2Cl_4	Ba_2F_4	Ba_2Cl_4
B_{2u}	123	50	135	68
E_g	163	94	157	92
A_{1g}	227	163	174	118
E_u	232	135	210	117
B_{1g}	270	164	259	157
B_{2g}	293	167	270	148
A_{2u}	333	190	317	176
E_u	348	223	320	199
A_{1g}	399	246	364	223

spectroscopy, especially of Raman spectroscopy, frequencies for the other dimers may soon be identified. The electron diffraction analysis of the heavier alkaline earth dihalides did not detect any amounts of dimers at the experimental conditions; thus, even if they were present, they could not be more than just a few percent of the vapor. However, with high-resolution matrix isolation spectroscopy even such small amounts could be detected.

Discussion

It is only in the last 10 years or so that the long-standing puzzle of the shape and structure of alkaline earth dihalides and dihydrides seems to have been resolved and the factors governing them understood. Concerning the monomeric molecules, it seems to be well established that both core polarization of the metal by the electronegative ligands and a small amount of covalent bonding involving the metal ($n - 1$) d orbitals are responsible for their bent shape. Thus, the smaller metal dihalides, BeX_2 and MgX_2, are all linear but all barium dihalides are bent. The calcium and strontium dihalides occupy intermediate positions; some of them (with the heavier halides) are linear, others (the fluorides) are bent, and $SrBr_2$ is best described as quasilinear with an extremely flat potential energy surface. CaF_2 and $SrCl_2$ are usually also considered to be quasilinear; even if their equilibrium geometry is unambiguously bent, their bending potential surface is extremely flat. Accordingly, their computational study is hindered by the extreme sensitivity of the results to basis set effects.[20a,b]

Only the lighter dimers of the alkaline earth dihalides (beryllium, magnesium, and calcium dihalide dimers) have been observed experimentally, and they were all found or supposed to have the typical double-halogen-bridged D_{2h} symmetry structure **1**.[26−28,41,42]

The emerging picture from the computational studies of the dimers of alkaline earth dihalides shows a correlation between the structure of the monomeric molecules and the structure of their dimers. All molecules that are linear as monomers prefer a planar arrangement around their metal centers in their dimers. Thus, the D_{2h} structure **1** is their most stable dimer, even if there are other structures with stable minima.

On the other hand, bent monomers prefer pyramidal metal coordination in their dimers. For all these molecules, the most stable dimer structure is the C_{3v} symmetry, triple-bridged structure **5**. It is easy to imagine that it requires much smaller rearrangement and thus less energy for a bent molecule to produce this structure than for a linear molecule. The larger the polarizability of the metal, the more favorable the anisotropic pyramidal coordination will be. This is supported by the fact that the stability of structure **5** compared to the D_{2h} structure **1** increases from Ca_2X_4 toward Ba_2X_4 within the same halogen series. Similarly, the more electronegative the halogen ligand, the more polarized the metal will be and the more stable is structure **5** compared with structure **1**.

The next two minimum structures for Sr_2F_4, Ba_2F_4, and Ba_2Cl_4 are structures **2** and **3**, also with pyramidal metal coordination, with structure **2** with the trans ligand arrangement being somewhat more stable than structure **3** with the cis ligand arrangement. The D_{2h} structure **1** is not even a minimum for these three molecules. For Ca_2F_4 and Sr_2Cl_4, structure **1** is still a minimum but with only slightly (8 and 13 kJ/mol, respectively) higher energy than structure **5**. These two are the extremely floppy, "quasilinear" molecules, representing intermediate cases between the linear/planar and bent/pyramidal systems.

Concerning the preference for pyramidal coordination of the heavy alkaline earth metals in three coordination, other examples can also be found in the literature as already noted in ref 15. Barium has a Ba−Ba−N angle of 158.3° in the dimeric complex $\{Ba[N(SiMe_3)_2]_2\}_2$ according to its X-ray diffraction study.[43] Similar complexes with lighter alkaline earth metals follow the same trend as the dihalides as far as the coordination of the metal is concerned. This situation parallels what is found for some monomeric organometallic compounds of alkaline earth metals. $Mg[C_5(CH_3)_5]_2$ has a linear Cp−Mg−Cp coordination,[13a] while the analogous molecules of Ca, Sr, and Ba are bent,[13a,b] just as is the case for the dihalides.

There are other examples of crystalline barium compounds whose structures resemble[15] our structure **5**, with three bridges and one terminal atom, such as the $Ba_2(OSiBu_3)_4(THF)$ complex.[44] Drake et al.[44] have suggested that it is advantageous for such ionic compounds to have three rather than just two bridging bonds to counter the large Coulombic repulsion of the two divalent cations.

Structure **6** with its high D_{4h} symmetry but very anisotropic metal environment is also a true minimum for all four molecules. This isomer is also favored by larger cation polarizability, so its stability can be expected to increase toward Ba, as is indeed the case. The smaller the anion, the more stable this structure will be with the same metal, since anion−anion repulsion destabilizes this structure.[15] Thus, among the four molecules, structure **6** is least unfavorable for Ba_2F_4, where it is only 65 kJ/mol higher in energy than structure **5**.

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