Structure and Stability of One-Dimensional (MX$_2$)$_n$ Polymers. A Band Structure Analysis

E. CANADELL*[†] and O. EISENSTEIN[‡]

Band structure calculations are used to analyze the structures of one-dimensional (BeCl$_2$)$_n$ and (BeMe$_2$)$_n$ polymers. The distortion away from the ideal tetrahedral angle at the beryllium atom, 98.2° in (BeCl$_2$)$_n$ and 114° in (BeMe$_2$)$_n$, is related to the existence of a lone pair on the bridging group or atom available for bonding with the Be centers. The analysis accounts correctly for the structures of other one-dimensional polymers such as (SiS$_2$)$_n$, (SiSe$_2$)$_n$, and fibrous (SiO$_2$)$_n$. The stability of these polymers is discussed in terms of the number of valence electrons per unit cell. It is demonstrated that 32 electrons per unit cell is the optimal number, which is in good agreement with the experimental evidence. New one-dimensional (MX$_2$)$_n$ polymers are proposed on the basis of this 32-electron rule.

In this paper we present a theoretical analysis of edge-sharing tetrahedral (MX$_2$)$_n$ periodic systems (M = main group metal, X = halide, alkyl, alkoxide, hydride) by means of band structure calculations. Our purpose is a better understanding of the structures and stabilities of these systems.

One-dimensional polymeric chains of MX$_2$ are commonly found for M = Be[1-5] and Mg[6-8] with various bridging X's. The best known examples are (BeCl$_2$)$_n$[1] and (BeMe$_2$)$_n$.[2] The simplest compound (BeH$_2$)$_n$[3] has been synthesized, although its structure could not be determined. With M = Be, X can also be an alkoxy group[4a] or a dissimilar pair (H, alkyl).[4b] Grignard reagents are believed to be polymeric.[8] (MgMe$_2$)$_n$[6] and (MgEt$_2$)$_n$,[7] which are also related to Grignard reagents, are well-characterized polymers.

The basic motif of these polymers is an edge-sharing tetrahedron as shown in **1**. A similar arrangement is known for

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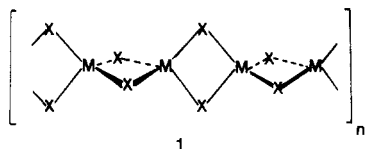
the silicon derivatives[9] (SiS$_2$)$_n$, (SiSe$_2$)$_n$, and fibrous (SiO$_2$)$_n$. A small-size polymer made of gallium and selenium (Ga$_6$Se$_{14}$)$^{10-}$ has been recently characterized.[10]

An interesting pattern emerges from the examination of the geometrical parameters of **1**. Although M is said to be tetrahedrally coordinated, the angle at the M center, ∠XMX, departs noticeably from the usual value of 109.47°. In (BeCl$_2$)$_n$ the ∠ClBeCl angle is 98.2°[1] while in (BeMe$_2$)$_n$ the ∠CBeC angle is 114°.[2] Similar distortions are observed in the silicon polymers;[9] the ∠XSiX angle is 98.8, 100, and 80° for X = S, Se, and O, respectively.

No detailed explanations have been offered for the above observations, although a relation between the ∠XMX angle and the amount of M–M bond was discussed.[2b] In (BeMe$_2$)$_n$ the large angle at the beryllium was correlated to the presence of a Be–Be bond.[2b] No similar suggestion was made for (BeCl$_2$)$_n$ or the isomorphous silicon chains.

The existence of a polymer of type **1** is attributed to an electron deficiency in the MX bonds. If M is a group 3 element such as Al or In, it is possible to obtain a structure (type **2**) of two edge-sharing tetrahedra[11] that is not electron deficient. No polymer of type **1** is known with M centers belonging to group 3. Interestingly, a type **1** polymer with alternating Al and Li centers (Et$_2$AlEt$_2$Li)$_n$ has been syn-
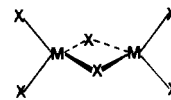
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thesized and structurally characterized.[12] As in other alkyl-bridge compounds previously mentioned, the CAlC angle is larger than the tetrahedral angle, namely, 112.1°.

Little is known about the electronic properties of polymers of type **1**. An ab initio band structure calculation of (BeH$_2$)$_n$ has been reported.[13] The energy bands were found to be sensitive to the nature of the basis set. The hydrides BeH$_2$, Be$_2$H$_4$, and Be$_3$H$_6$ have been investigated by means of ab initio calculations including electron correlation.[14] It has been found that BeH$_2$ has a strong tendency to polymerize in linear chains. The polymerization energy has been estimated at 40 kcal/mol. An ionic model of beryllium, magnesium, and calcium dihalides has been done.[15] The coordination number of BeCl$_2$ could not be correctly reproduced, and the M–M distances

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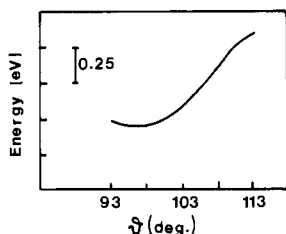
Figure 1. Total energy per unit cell of (BeCl$_2$)$_n$ as a function of the ClBeCl (θ) angle.

have been found exaggerated compared to the experimental values.

In this paper we present a theoretical analysis of systems of type **1** based on band structure calculations. The geometric distortion at the M center and its relation to the electronic characteristics of the bridging X is analyzed by using the methodology of Hoffmann,[16] Whangbo[17] and Burdett.[18] The propensity for any MX$_2$ to polymerize is discussed and related to the number of valence electrons in the chemical unit MX$_2$.

Theoretical Procedure

The tight-binding method[19] of band structure calculation based upon the extended Hückel formalism was used. Given a set of basis atomic orbitals $\{\chi_\mu\}$ for the atoms of a unit cell, the set of the Bloch basis orbitals $\{b_\mu(\mathbf{k})\}$ are formed as

$$b_\mu(\mathbf{k}) = N^{-1/2}\sum_l e^{i\mathbf{k}\cdot\mathbf{R}_l}\chi_\mu(r - \mathbf{R}_l) \tag{1}$$

where $\mathbf{k}$ is the wave vector and $\mathbf{R}_l = l\cdot\mathbf{d}$, with $\mathbf{d}$ being the primitive vector. With these Bloch basis orbitals the extended Hückel method leads to the eigenvalue equation

$$H(\mathbf{k})\,C(\mathbf{k}) = S(\mathbf{k})\,C(\mathbf{k})\,e(\mathbf{k}) \tag{2}$$

where $H_{\mu\nu}(\mathbf{k}) = \langle b_\mu(\mathbf{k})|H_{\text{eff}}|b_\nu(\mathbf{k})\rangle$ and $S_{\mu\nu} = \langle b_\mu(\mathbf{k})|b_\nu(\mathbf{k})\rangle$. The solution of this eigenvalue problem results in LCAO crystal orbitals $\psi_n(\mathbf{k})$

$$\psi_n(\mathbf{k}) = \sum_\mu C_{n\mu}(\mathbf{k})\,b_\mu(\mathbf{k}) \tag{3}$$

and eigenvalues $\epsilon_n(\mathbf{k})$. The band structure is then determined by performing the above calculation for various values of $\mathbf{k}$ (usually within the first Brillouin zone; $-0.5\mathbf{K} \leq \mathbf{k} \leq 0.5\mathbf{K}$ where $\mathbf{K} = 2\pi/\mathbf{d}$). The parameters of the extended Hückel calculation and geometries are given in the Appendix.

A unit cell of **2** contains two BeX$_2$ units. In our calculations lattice sums were carried out to the third nearest neighbors (i.e., $l = -3, -2, -1, 0, 1, 2, 3$ in eq 1) and eq 2 was solved at $\mathbf{k} = 0.0\mathbf{K}, 0.1\mathbf{K}, 0.2\mathbf{K}, 0.3\mathbf{K}, 0.4\mathbf{K}$, and $0.5\mathbf{K}$.

(BeCl$_2$)$_n$ Chain

Figure 1 shows the variation of the total energy per unit cell as a function of the ClBeCl (θ) angle. A minimum is reached at 97°, an angle definitely more acute than the tetrahedral one and close to the experimental value of 98.2°.

To explain this distortion, we turn our attention to the band structure shown in Figure 2. In our coordinate axis the xz and yz planes are symmetry elements of the crystal. Each crystal orbital has been labeled according to its symmetry with respect to these two planes. The SA and AS crystal orbitals are degenerate for all values of the wave vector $\mathbf{k}$ due to the
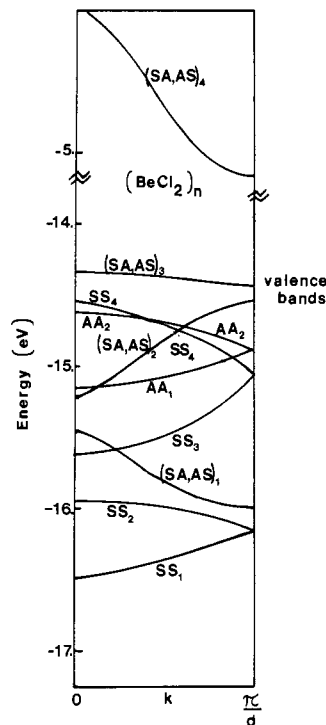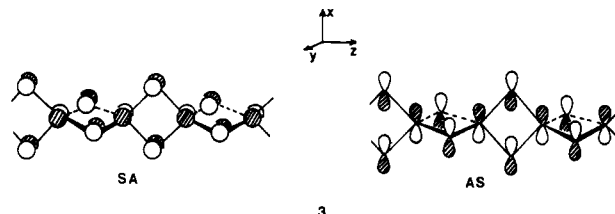
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Figure 2. One-dimensional band structure for the (BeCl$_2$)$_n$ chain. The four lower bands have been omitted.

equivalence of xy and yz planes. The top ($\mathbf{k} = 0$) of the degenerate valence bands (SA,AS)$_3$ is shown in **3** as an ex-

ample of this set of (SA,AS) degenerate crystal orbitals. The SS crystal orbitals (Figure 2) pair up at the zone edge ($\mathbf{k} = \pi/\mathbf{d}$) as do the AA ones. The SS bands, which are going to have a major importance in the story, deserve special attention. SS$_4$ is the highest SS occupied band. At the zone center ($\mathbf{k} = 0$) it is the in-phase combination of p$_z$ atomic orbitals on each center as shown in **4**. At the zone edge ($\mathbf{k} = \pi/\mathbf{d}$) the
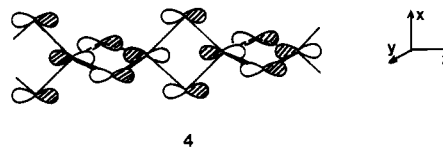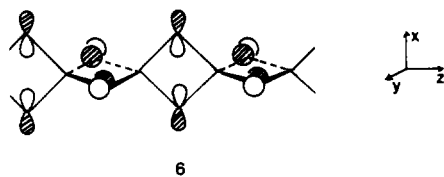

crystal orbital introduces p$_y$ atomic orbitals on the pair of chlorine atoms contained in the yz plane, **5**. This increases
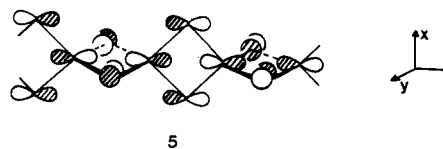

the bonding properties of the crystal orbital at $\mathbf{k} = \pi/\mathbf{d}$ and consequently the slope of the SS$_4$ band is negative.

The bottom of SS$_3$ ($\mathbf{k} = 0$), **6**, is made mostly of chlorine atomic orbitals: p$_x$ for the chlorine atoms in the xz plane; p$_y$ for the chlorine atoms in the yz plane. The two chlorine atoms of the xz plane form a σ_x bond, and the two chlorine atoms of the yz plane form a σ_y bond. **6** can be adequately described

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as the in-phase combination of $(\sigma_x - \sigma_y)$. It is clear that lower in energy there is a $(\sigma_x + \sigma_y)$ crystal orbital, **7**. This is actually

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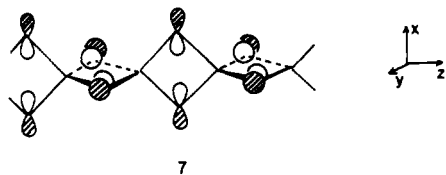
the top of the SS_2 band (**k** = 0). The bottom of SS_1 (**k** = 0) is an in-phase mixing of chlorine p_z and beryllium atomic orbitals, **8**.

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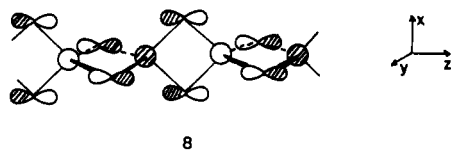
In order to trace the bands that are responsible for a small θ angle, we have calculated the mean energy value of each band at θ = 98.2 and 109.47° (Figure 3). Figure 3 is therefore the solid-state equivalent of a Walsh diagram.[16b] When multiplying this mean energy value by the number of electrons in this band, one obtains the contribution to the total energy per unit cell of each band. The result is illuminating. Three SS bands are much more stable at 98.2° than at 109.47°. Only SS_2 is unaffected by the change in θ. Among the bands of other symmetries, only AA_1 is significantly destabilized at 98.2°. Nevertheless, the greater stability of the SS bands at 98.2° overcomes the destabilizing influence of AA_1. Consequently, a small θ angle is favored.

Our goal is now to understand why the SS bands are more stable at a smaller angle. It turns out that it is sufficient to analyze the behavior of the band at one **k** point (**k** = 0). This is due to the fact that the change in θ results only in a translation of the whole band toward lower or higher energy values.

Consider SS_4 (**4**). Decreasing θ has three consequences. It increases the σ-bonding overlap between Cl and Be p_z orbitals. It also increases the bonding overlap between the two p_z orbitals of two chlorine atoms attached to the same beryllium atoms. It finally decreases the antibonding overlap between the Be–Be p_z atomic orbitals. All these factors favor a small θ value.

An analogous reasoning can be done for SS_3 (**5**) and SS_1 (**7**). In both cases the decrease in θ increases significantly the bonding between Be and Cl and/or between the Cl centers. In contrast, SS_2 (**6**) does not vary with θ. This crystal orbital is adequately described at **k** = 0 as the in-phase combination of $(\sigma_x - \sigma_y)$. Decreasing θ increases the antibonding interaction between σ_x and σ_y. Simultaneously, σ_x and σ_y become more bonding. Both effects cancel each other.

AA_1 is destabilized by the decrease in θ. As is apparent in **9**, the antibonding interaction between two Cl atoms in the

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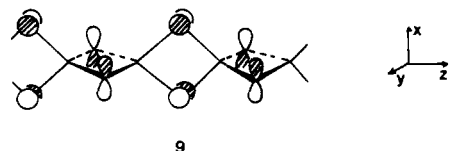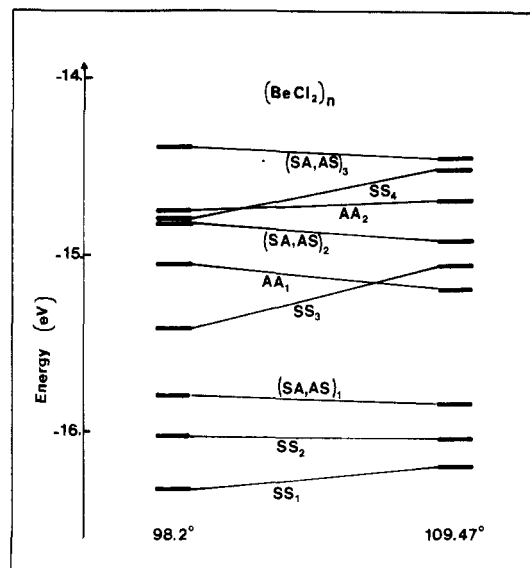
same plane is enhanced and the bonding interaction between

Figure 3. Mean energy value of each band at θ = 98.2 and 109.47° for $(BeCl_2)_n$. θ = ∠ClBeCl angle.
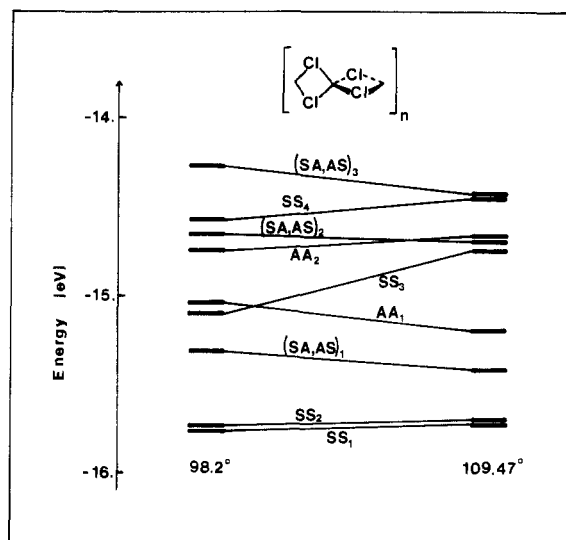

Figure 4. Mean energy value of each band at θ = 98.2 and 109.47° for $(Cl_4{}^{4-})_n$. See text for definition of the system.

pairs of chlorine atoms in adjacent planes decreases. The first effect dominates, but the overall effect remains small because of the nature of the overlap (π type) between the chlorine orbitals.

The SS bands are therefore responsible for the acute ∠ClBeCl angle. Comparing **4** to **6** and **7**, one sees two different types of SS bands. **4** derives its bonding character mostly from Be–Cl interactions. In contrast, **6** and **7**, which have a negligible beryllium contribution, can be considered as originating from an infinite chain of Cl⁻ ions. Since $(BeCl_2)_n$ has a strong ionic character, we calculated a polymeric chain of Cl⁻ ions in order to study the possibility that the experimental geometry was due to the interaction between ionic chlorine atoms. The geometry was kept identical with that of $(BeCl_2)_n$. We define the θ angle using a dummy atom in place of the Be. We found that the total energy per unit cell slightly favors the tetrahedral angle. The solid-state Walsh diagram is shown in Figure 4. The comparison of Figures 3 and 4 points out the role of the beryllium atom.

In the absence of Be, SS_4 is not as much stabilized by the decrease in θ. This originates from the absence of the Be–Cl σ bonding, which is the main bonding interaction in SS_4. In contrast, SS_3, in which the beryllium contribution is negligible,

Table I. Mulliken Overlap Population in $(BeCl_2)_n$ and $(BeMe_2)_n$ at Their Experimental Geometry

	X = Cl	X = Me
Be–Be	−0.04	0.13
Be–X	0.41	0.20
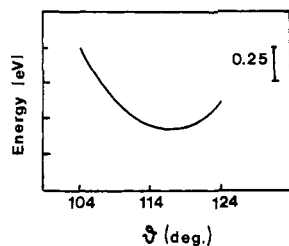
Figure 5. Total energy per unit cell of $(BeMe_2)_n$ as a function of the CBeC (θ) angle.

behaves very similarly with or without the beryllium. It is clear that in the absence of Be the chain is losing some of the factors favoring an acute θ angle. In addition, unfavorable factors are augmented. For instance, the highest occupied band $(SA,AS)_3$ is much more destabilized at a small θ value when Be is removed. If one takes off the beryllium contribution from **3**, the behavior of the crystal orbital is dominated by the strong antibonding σ^* type interaction between the Cl atoms.
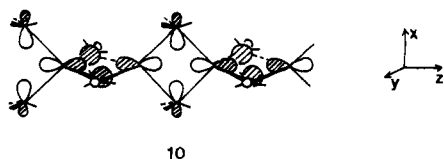
The small $\angle ClBeCl$ angle in $(BeCl_2)_n$ is therefore due to an optimization of the Be–Cl bonding. At that point, we would like to know whether there is any sort of Be–Be bond. The above analysis suggests that the polymer is held together more by Be–Cl bonds than by Be–Be ones. A Mulliken overlap population analysis (Table I) supports this hypothesis. The Be–Be overlap population is weakly negative while that of Be–Cl is large and positive 0.4. Therefore, this analysis indicates that there is no Be–Be bond in $(BeCl_2)_n$.

$(BeMe_2)_n$ Chain

Figure 5 gives the total energy per unit cell as a function of the $\angle CBeC$ (θ) angle. The minimum occurs at 118°, an angle definitely larger than the tetrahedral one, in good agreement with the experimental value (114°). The band structure at the experimental θ value is shown in Figure 6. The symmetry labels of the bands are similar to those of $(BeCl_2)_n$.

The solid-state Walsh diagram is shown in Figure 7 for θ = 114 and 109.47°. Most of the crystal orbitals are insensitive to the change in the θ value. SS_4 is weakly stabilized at smaller θ, and the highest occupied bands $(SA,AS)_3$ behave in the opposite way. It is difficult to attribute the preference for a large θ to any particular band or set of bands. The effect is spread over all of them. What makes $(BeMe_2)_n$ different from $(BeCl_2)_n$ is the absence of a sizable stabilization of the SS bands for a smaller θ value. This is clearly at the origin of the different geometrical features of the two chains.
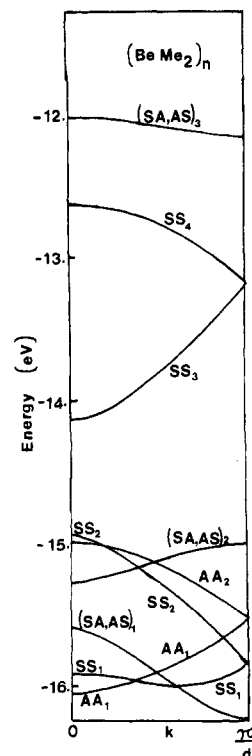
The bonding patterns of the SS bands of $(BeMe_2)_n$ are different from those of $(BeCl_2)_n$. SS_4 at k = 0 (**10**) consists of the p_z orbital of the beryllium atom and of the in-phase combination of the sp^3 hybrids of the CH_3 groups.


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This orbital is not much affected by a change in θ; bringing the CH_3 groups together forces the Be atoms to move apart. The increase in CH_3–CH_3 bonding is compensated by a decrease in Be–Be bonding. As the orbital is more on the Me

Figure 6. One-dimensional band structure for the $(BeMe_2)_n$ chain. The four lower bands have been omitted.

Figure 7. Mean energy value of each band at θ = 109.47 and 114° for $(BeMe_2)_n$. θ = $\angle CBeC$ angle.

group than on the electropositive Be, it tends to favor very slightly a smaller θ angle.

The AS crystal orbital of the valence $(SA,AS)_3$ set is shown in **11** (k = 0). It is mostly the out-of-phase combination of

the sp^3 hybrids of the CH_3 groups and thus favors a larger θ angle.
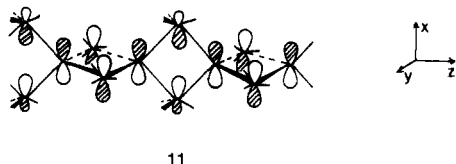
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The Mulliken overlap population analysis confirms the accepted idea that there is a Be–Be bond in $(BeMe_2)_n$. As shown in Table I, the Be–Be overlap population is noticeable (0.13) and the Be–Me bond is much weaker than the Be–Cl one (0.2 vs. 0.4).

One can relate the nonexistence of a Be–Be bond in $(BeCl_2)_n$ and the occurrence of a Be–Be bond in $(BeMe_2)_n$ to the shapes of the SS bands and especially to that of SS_4. It is also, naturally, directly related to the value of the θ angle. At $\mathbf{k}$ = 0, in $(BeCl_2)_n$ the crystal orbital of SS_4 is Be–Be antibonding (4), while in $(BeMe_2)_n$ it is bonding (10). Therefore, SS_4 contributes to the destruction of the Be–Be bond in $(BeCl_2)_n$ and to its buildup in $(BeMe_2)_n$. A related analysis has been done by Hoffmann and co-workers in their discussion of multiple metal–metal bonds.[21]

Geometry of Edge-Sharing Tetrahedral $(MX_2)_n$ Chains and Existence of an M–M Bond

We now have in our hands all the elements to propose a general rule to predict the $\angle XMX$ angle and the existence of an M–M bond in any edge-sharing tetrahedral $(MX_2)_n$ (M = main group element). It depends on the pattern of the valence orbitals of X.
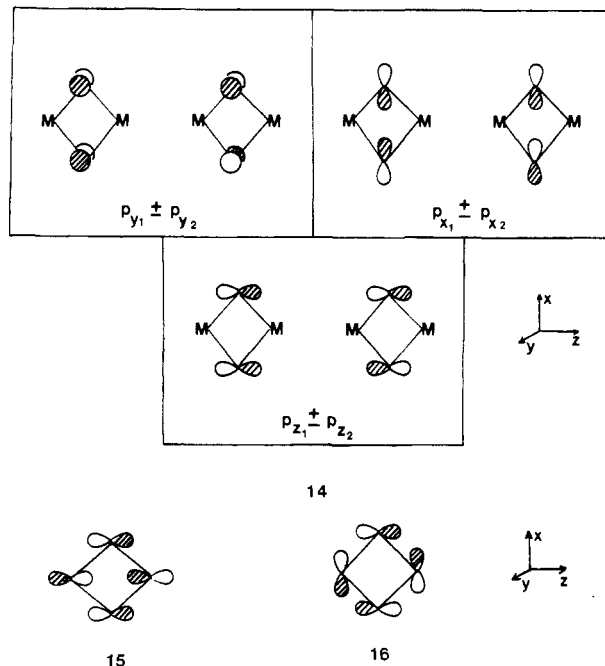
CH_3 has three valence orbitals, a low-lying set of degenerate π_{CH_3} orbitals that are not capable of any strong bonding with the neighboring M atoms and a σ hybrid that in contrast can enter into strong bonding with the M atoms. From two CH_3 groups, two valence orbitals $\sigma_1 + \sigma_2$ and $\sigma_1 - \sigma_2$ are made. $\sigma_1 + \sigma_2$ is stabilized by $(p_{z1} - p_{z2})$, **12**. $\sigma_1 - \sigma_2$ has the adequate symmetry to overlap with $(p_{x1} + p_{x2})_M$ [or $(p_{y1} + p_{y2})_M$, if $\sigma_1 - \sigma_2$ is in the yz plane], **13**. **12** is insensitive to θ and **13** favors a larger θ angle.

12   13

The situation is very different for X = Cl, which has three valence p atomic orbitals available for bonding with M (the very deep s orbital can be neglected). From two chlorine atoms, one derives six symmetry-adapted orbitals: $(p_{x1} \pm p_{x2})$, $(p_{y1} \pm p_{y2})$, $(p_{z1} \pm p_{z2})$ (**14**). $(p_{y1} + p_{y2})$ can be neglected because it makes only π type bonding with the M atoms. $(p_{y1} - p_{y2})$ does not find any match with the symmetry-adapted combination of M atomic orbitals, provided there are no d atomic orbitals on M. Neither of these two orbitals have any strong influence on θ. $(p_{x1} \pm p_{x2})$ are analogous to $(\sigma_1 \pm \sigma_2)$ for the Me-bridged system and favor a larger θ value. $(p_{z1} + p_{z2})$ is clearly the crucial orbital. It overlaps with $(p_{z1} + p_{z2})_M$ as shown in **15** and strongly favors a smaller θ value. $p_{z1} - p_{z2}$, which overlaps with $(p_{x1} - p_{x2})_M$ as shown in **16**, is quite insensitive to θ.

(20) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179; **1962**, *37*, 177, 2872.

(21) Shaik, S.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 1194. Shaik, S.; Hoffmann, R.; Fiesel, C. R.; Summerville, R. H. *Ibid.* **1980**, *102*, 4555.

$p_{y_1} \pm p_{y_2}$ $p_{x_1} \pm p_{x_2}$

$p_{z_1} \pm p_{z_2}$

14

15   16

We have therefore sorted out the factor responsible for the observed $\angle XMX$ angle. If X has valence orbitals available for bonding with M and parallel to the propagation axis, a small θ angle is expected. This is the case for $(BeCl_2)_n$, θ = 94.8°, $(SiO_2)_n$, θ = 80°, $(SiSe_2)_n$, θ = 100°, and $(SiS_2)_n$, θ = 98.8°, in which each bridging atom makes use of its p_z lone pair. One should expect the same behavior for alkoxy, thioalkoxy, and phosphido bridging groups. To our knowledge no structural information is yet available on such systems. In contrast, if the bridging group has no orbital available for bonding and parallel to the propagation axis, one should expect a large θ angle. This should be the case for all alkyl groups, amines, phosphines, and hydrides. We are looking forward to new structural data with which to confront our predictions.

The existence of an M–M bond is easily deduced from the above analysis. If X has no lone pair parallel to the propagation axis, one should expect an M–M bond coming mainly from the interactions shown in **12**. If X has a lone pair parallel to the propagation axis, the bonding pattern shown in **15** contributes to the destruction of an M–M bond.

Polymeric vs. Dimeric Structures

In $(BeCl_2)_n$ the highest occupied band is the $(SA,AS)_3$ degenerate set. Replacing Be by Al adds two electrons per unit cell. This would put electrons in the $(SA,AS)_4$ bands, which are very high in energy. This is a very unfavorable situation, and no polymer of type $(AlCl_2)_n$ can exist.

An alternative and illuminating way to discuss the relative stabilities of polymeric and dimeric edge-sharing tetrahedral species is to consider the interaction between a $(BeX_2)_2$ fragment, i.e., a unit cell of the polymer, and another unit cell or two terminal Y groups.

The molecular orbitals of $(BeX_2)_2$ are easily derived from those of a bent BeX_2 unit. The occupied orbitals are mostly centered on X. The low lying MOs are the σ and p_x orbitals **17** centered on Be. When two BeX_2 units are linked together,
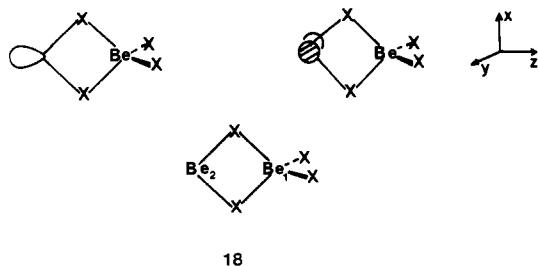

17

the occupied orbitals of the X centers push σ and p_x of Be to high energy. Simultaneously, a new set of low-lying empty orbitals (σ and p_y) are centered on the terminal Be_2, **18**. It

18

is clear that the $(BeX_2)_2$ unit can be linked to an additional unit with the same important results: two low-lying empty orbitals centered on the terminal Be atom are formed. As long as these orbitals are empty, the chain can continue to grow.

Consider now the interaction of two Y groups with $(BeX_2)_2$, each Y group entering as a Lewis base. The symmetric and antisymmetric combinations of the Y orbitals are both doubly occupied and have the symmetry of the LUMOs of $(BeX_2)_2$, **19**. The electron configuration of $Y_2 Be_2X_4$ is satisfied, and

19
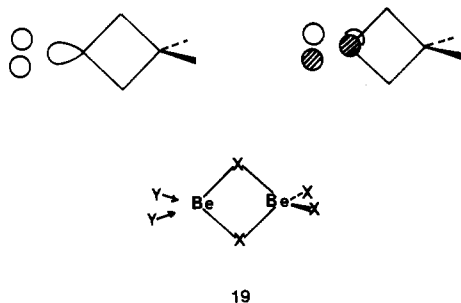
the polymerization has come to an end. Such a termination process can occur for any size of the $(MX_2)_p$ cluster. That is the case for $Ga_6Se_{14}^{10-}$, which is formally made up of three $(GaSe_2)_2^{2-}$ and two Se^{2-} units. Why does this polymerization stop at some point? This is a difficult question that we cannot answer without better quality calculations.

The above analysis applies also to Al_2Cl_6 if it is considered to be made up of two Cl atoms and an $(AlCl_2)_2$ fragment. In $(AlCl_2)_2$, the σ orbital centered on the terminal Al is occupied. There is only one empty orbital, namely p_y. It is clear that $(AlCl_2)_2$ cannot bind to another equivalent unit without putting electrons in very high-lying orbitals that cannot be stabilized by terminal groups. In contrast, $(AlCl_2)_2$ has the adequate number of electrons to interact with two Cl atoms, each Cl atom coming with one electron.

Clearly, a polymer is to be found if the valence bands are the $(SA,AS)_3$ ones. A system with less electrons would not be stable. In order to fill the bands up to the necessary level, one needs 32 electrons per unit cell, that is 16 per MX_2 chemical unit. This is precisely the number of valence electrons

of $(BeCl_2)_n$, $(BeMe_2)_n$, and $(SiX_2)_n$ with X = O, S, Se. $(AlEt_2LiEt_2)_n$ also has 32 valence electrons (Et should be replaced by Me for electron count purposes), and $(Ga_6Se_{14})^{10-}$ likewise obeys the above electron rule. Considering two terminal Se as Se^{2-}, we are left with a system $(GaSe_2)_6^{6-}$, which has 16 electrons per $(GaSe_2)^-$ unit. Using this simple electron-count device, one can think of other polymers that are still to be made. The oxygen atom has the same number of valence electrons as CH_2 or NH. Polymers like $(Si(CH_2)_2)_n$ and $(Si(NH)_2)_n$ are feasible on the sole basis of electron count.

Many other chains can be proposed by using the isolobal analogy.[22] Nevertheless a word of caution is in order here. It must be recalled that these polymers are very sensitive to steric factors. $BeEt_2$, $Be(i-Pr)_2$, and $Be(t-Bu)_2$, although equivalent to $BeMe_2$, are dimeric.[23] Other geometries may be preferred. Another problem is that the polymer can stop for any reason using terminal groups, which satisfies a closed-shell structure as in the gallium–selenium chain. We are aware that these factors are not yet understood, but we believe that the above electron-count rule may be useful for designing new polymers of type **1**.

Appendix

The exponents and parameters for beryllium and chlorine were taken from Celementi and Roetti[24] and from Hinze and Jaffe,[25] respectively. The modified weighted Wolfsberg–Helmholtz formula was used.[26] Experimental structural data were used for the bond distances: Be–Cl, 2.02 Å; Be–C, 1.93 Å; C–H, 1.09 Å.

atom	orbital	H_{ii}, eV	ζ
Be	2s	−10.0	0.975
	2p	−6.0	0.975
Cl	3s	−24.2	2.35
	3p	−15.0	2.039

Registry No. $BeCl_2$, 7787-47-5; $BeMe_2$, 506-63-8.

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