

Building Bridges: Rationalizing Structural Preferences in the Group 2 dihalide
Trimer Systems: $(MX_2)_3$: M = Be, Mg, Ca, Sr, Ba; X = F, Cl, Br, I.

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Abstract:

As part of the larger study of the structural preferences of metal halide compounds, we investigate the bonding patterns and structural preferences of lower order $(MX_2)_n$ oligomers, focusing in this part of the on the study on trimers of the group 2 metal dihalides. The heavier group 2 dihalide compounds are well known to deviate from the predicted VSEPR linear model and form bent monomers. The question posed in this poster is how do the structural preferences in different parts of the series of group 2 dihalides evolve beyond the monomers and dimers to the next highest level, the trimers. Starting from a number of guess geometries, links between the bending in the monomers, D_{2h}/C_{3v} symmetry in the dimers and $D_{2d}/C_s/D_{3d}$ symmetry in the trimers have been identified. At the B3PW91 computational level, linear monomers prefer a doubly bridged D_{2h} dimeric structure as well as the D_{2d} trimer structure. The bent monomers all form the D_{2h} dimeric structure but show variance in their trimer preference. SrF_2 , $SrCl_2$, and BaF_2 prefer the C_s trimer structure, while $BaCl_2$, $BaBr_2$, and BaI_2 favor the D_{3d} trimeric structure. There is also a relationship between the structural trends in the lower level oligomers and the extended solids. We find that the extended solids obtained from the linear molecules show a marked preference for low metal coordination numbers, CN, ($CN \leq 6$) and the solids formed from the bent monomers prefer a higher metal coordination ($CN > 6$). We explore the reasons for these correlations in this poster.