

# Parsing the Bonding in the Aluminum Trichloride Dimer

By Joel M Williams (text and images ©2015)

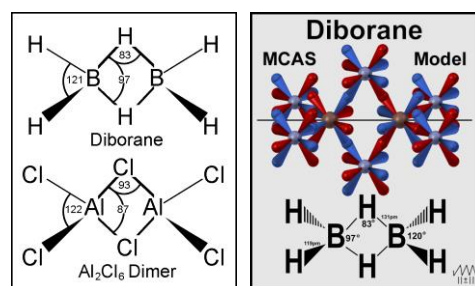
[CLICK for 'Parsing the spdf Electron Orbital Model' which includes the MCAS Model](#)

## Abstract

*The shorter distance between the bridging chlorine atoms compared with that between the aluminum atoms is discussed in terms of the  $sp^3$  hybrid model and the MCAS atomic model.*

## Lewis Acids and their Dimers

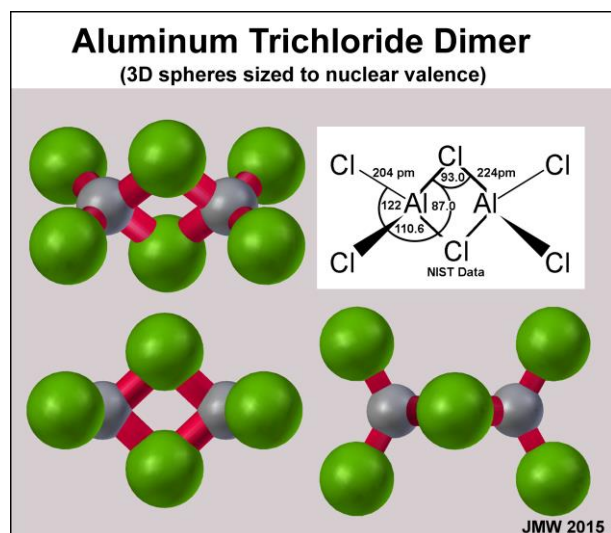
Boron and aluminum have just three (3) valence electrons and form trivalent molecules. Typical ones are  $BH_3$ ,  $BCl_3$  and  $AlCl_3$ . The latter are Lewis acids (after G.N. Lewis<sup>1</sup>); i.e., they lack an octet of electrons around the metal atom and accept another atom with electrons to address the problem. One way these molecules satisfy the problem on their own is to form dimers. The basic structure of the dimers of  $BH_3$  and  $AlCl_3$  are shown in first figure on the right. One of the non-metal atoms from each molecule forms a "bridge" to the other. The situation is explained by accepted  $sp^3$  bonding methodology when halogens do the bridging, but such is not the case when the bridge is hydrogen. To explain why hydrogen can form a bridge, 3-centered bonds were invoked. Of course, no such aberration is necessary, if hydrogen is treated in the same



manner as other elements; that approach has been covered for diborane by the author elsewhere<sup>2</sup>. The MCAS electron structure of atoms treats hydrogen just like every other atom in the periodic table! The MCAS model of diborane is given in the second figure. This short treatise parses the aluminum chloride dimer structure from the viewpoint of electron distribution and the angles in the rhombus.

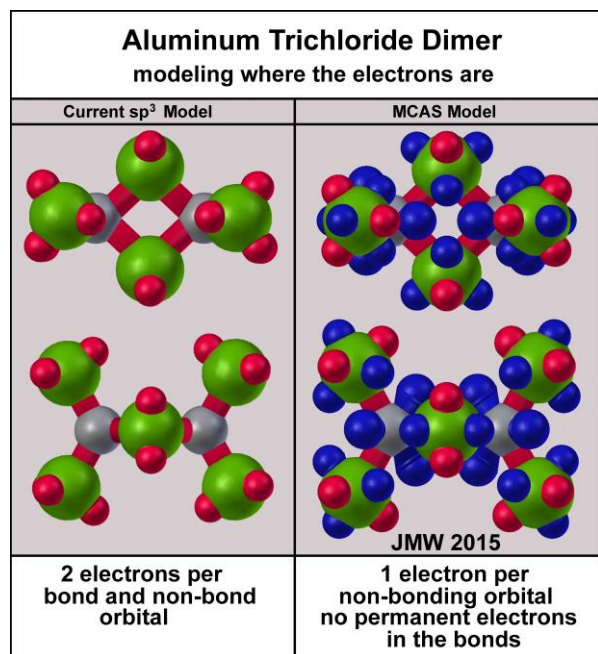
## Aluminum Trichloride Dimer Electronic Structure

The figure on the right shows the arrangement of the atoms of the aluminum trichloride dimer. The model was created with Blender software<sup>3</sup> using NIST<sup>4</sup> angle and bond lengths. The size of the atoms was made to reflect their "positiveness": 7 for Cl to 3 for Al. The first thing of note is the greater Al-Cl-Al angle ( $93^\circ$ ) compared to the Cl-Al-Cl angle ( $87^\circ$ )<sup>\*</sup>. This is quite concerning considering the  $7/3 = 2.3x$  greater valence charge for the chlorine atoms! With this noticed, let's look at how the electrons play a part in the matter.

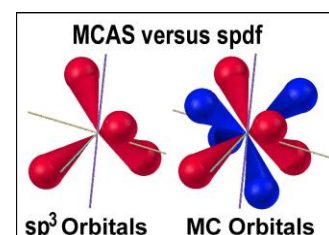


\* Two websites report  $101^\circ$  for the Al-Cl-Al angle and  $79^\circ$  for the Cl-Al-Cl angle. These non-NIST values appear in an "images" web search. There are no references to the values in the related web site: a) <http://www.tutorvista.com/content/chemistry/chemistry-iv/p-block-elements/reactivity-elements.php>; b) <http://www.wonderwhizkids.com/index.php/chemistry/metals-and-non-metals/boron-family> (the image is several pages deep in the "boron family" using the "arrow").

In the current spdf electron orbital and bond modeling approach, electrons are to be paired. For  $\text{Al}_2\text{Cl}_6$ , there are 48 valence electrons (3 per each Al and 7 per each chlorine atom). Each of the atoms is  $\text{sp}^3$ -hybridized<sup>5</sup>. The 8 bonds contain 16 of them (8 pairs) with 6 allocated (in 3 pairs) to each terminal chlorine and 4 allocated (in 2 pairs) to each bridging chlorine. The imagery is shown in the left portion of the figure on the right. Paired electrons occupy each of the red locations. The atomic radius<sup>6</sup> of aluminum (118pm) is larger than that of chlorine (79pm) as the orbital extent is less restricted with its lower valence positive charge (3 vs 7). For the purpose of the conventional  $\text{sp}^3$  bonding methodology, this difference is confined to the Al-Cl bonds. With the electrons in their assigned places, it is not obvious why the distance between the bridging Cl atoms (308pm) is less than that between the two Al atoms (325pm). Modeling programs make it so, however. Such reasoning is not intuitive from the typical  $\text{sp}^3$  model shown.

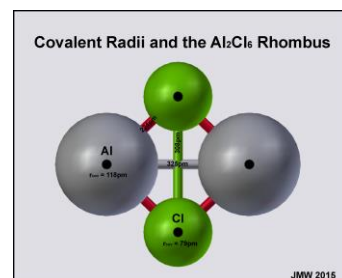


Consider now the interactions that occur when the  $\text{Al}_2\text{Cl}_6$  dimer is handled by MCAS model<sup>5</sup>. The pertinent orbitals of the two approaches are shown in the figure on the right. Both models have bonds created by joining orbitals from two different atoms. Unlike the  $\text{sp}^3$  hybrid model wherein the bonds are filled with 2 paired electrons, the bonds of the MCAS model have NO PERMINENT electrons in the overlapped orbital bond. Each lobe contains a maximum of 1 electron. The MCAS concept is that a bond represents the elimination of electron deficiency for each atom. Without delving too much further into the MCAS approach, suffice it to say at the moment that the model has maximum uniform distribution of electrons around the nucleus with one 4-lobed set dedicated solely to the atom (non-bonding) while the other 4-lobed set provides interatomic bond networking. The red orbital units are used for the bonds of both modeling approaches for consistency. In the extreme, the MCAS models leads to conduction (connected red) and non-conduction (non-connected blue) bands. This is envisioned as the case for silicon semiconductors<sup>7</sup>.



The two modeling approaches are presented side-by-side above. The broader coverage of the nuclei (and molecule in general) with electron presence is clearly far greater for the MCAS model with all the orbitals (red and blue) containing an electron. Unlike in the  $\text{sp}^3$  model, the red orbitals form an electron-deficient continuum. No electrons are permanently in the regions between the nuclei, but, just as with the  $\text{sp}^3$  model, 16 electrons are in the bonding network; they are just at the termini. The non-bonding electrons now become a factor in the electrostatic interactions. The non-bonding orbitals of the aluminum atoms are larger than those of the chlorine atoms (118 vs 79pm atomic radius). There is more e-e repelling between the Al atoms than between the Cl atoms. The center of the rhombus has more electron presence which helps to counter the Cl-Cl p-p repelling by adding e-p attraction. The shorter Cl-Cl distance vs the Al-Al distance is more rational with the MCAS model.

The covalent radii of Al and Cl are placed on the rhombus portion of the dimer in the figure on the right. Unlike the four terminal chlorine atoms that can rotate, these atoms do not. While the  $\text{sp}^3$  model confines valence electrons to the bonds, the MCAS model does not and thus mimics the general expanse of the covalent radii. The reader is left to compare this figure with the imagery of the two models presented earlier.



## REFERENCES

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- <sup>1</sup> *The Lewis Definition of Acids and Bases*, <http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch11/lewis.php>; Gilbert N. Lewis, [http://en.wikipedia.org/wiki/Gilbert\\_N.\\_Lewis](http://en.wikipedia.org/wiki/Gilbert_N._Lewis)
- <sup>2</sup> *Nixing the 3-Center Orbital Bond Concept of Diborane*, Joel M Williams, [http://pages.swcp.com/~jmw-mcw/Nixing\\_the\\_3-center\\_Orbital\\_Bond\\_Concept\\_of\\_Diborane](http://pages.swcp.com/~jmw-mcw/Nixing_the_3-center_Orbital_Bond_Concept_of_Diborane), <http://vixra.org/abs/1403.0960>, or <http://gsjournal.net/Science-Journals/Essays/View/5395>
- <sup>3</sup> Blender Version 2.70; the current version is 2.73, <http://www.blender.org/>
- <sup>4</sup> *Listing of experimental data for Al<sub>2</sub>Cl<sub>6</sub>*, <http://cccbdb.nist.gov/exp2.asp?casno=13845120>
- <sup>5</sup> *Parsing spdf Orbital Hybridization and Simple Bonding*, Joel M Williams, [http://pages.swcp.com/~jmw-mcw/Parsing\\_spdf\\_orbital\\_hybridization.html](http://pages.swcp.com/~jmw-mcw/Parsing_spdf_orbital_hybridization.html), <http://vixra.org/abs/1405.0216>, or <http://www.gsjournal.net/Science-Journals/Essays/View/5489>
- <sup>6</sup> *Atomic Radius for the Elements*, <http://www.periodictable.com/Properties/A/AtomicRadius.v.wt.html>
- <sup>7</sup> *Crystalline Carbon and Silicon: Covalent or Ionic?*, Joel M Williams, [http://pages.swcp.com/~jmw-mcw/Crystalline\\_carbon\\_and\\_silicon-Covalent\\_or\\_Ionic.htm](http://pages.swcp.com/~jmw-mcw/Crystalline_carbon_and_silicon-Covalent_or_Ionic.htm), <http://vixra.org/abs/1403.0296>, or <http://gsjournal.net/Science-Journals/Essays/View/5363>