

Where are the lone pairs? QC and QCT

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Defining detailed chemical structure is one of the most crucial tasks of chemistry. The history of chemistry is full of controversies about specific chemical structures, depending on the definition of connectivity, deciding where to place a bond and where to locate a lone pair. However, nowadays, there are two complementary tools that help us define chemical structure unambiguously: quantum crystallography (QC) and quantum chemical topology (QCT).

QC allows us to determine the electron density, density matrices and wavefunction [a molecular orbital set at the density functional theory (DFT) level], and fit these quantities to the experimental data (Genoni & Macchi, 2020). In recent decades, several methods have been developed to perform the fitting following on from the original one presented by Jayatilaka & Grimwood (2001). Once the quantum quantities are obtained, an analysis can be made by their topology, following the general recipe established by Bader, *i.e.* QCT (Bader, 1990). In general, given a physical quantity and its analytical definition, the topological analysis gives descriptors that can be used to define chemical concepts that can be proved by comparing them to the experimental results. QCT helps study crystal packing, molecular recognition and dynamic structures. I remember being present during a discussion between Professors Bader, Gillespie and Silvi about the Laplacian of electron density and the electron localization function (ELF) applied to chemical bonding in hypervalent molecules (Noury *et al.*, 2002). In that passionate discussion about the origins, definitions, qualities and defects of both functions, Professor Silvi mentioned to Professor Bader that he had just followed his topological recipe to develop the ELF analysis. These two functions allow the localization of lone pairs and the determination of the nature of the interaction between two atoms (Bader *et al.*, 1996). However, the Laplacian of electron density provides more detailed information, mainly because one can define a topological object called an atomic graph, which describes quantitatively the polarization of the atomic valence shell.

In the article presented by Guzmán-Hernández & Jancik (2024), QC and QCT were used to analyze tetrameric $(\text{SeCl}_4)_4$, which presents a heterocubane structure with bridged chlorines (Cl_b) at four vertices and SeCl_3 at the other four vertices. SeCl_3 defines the edge-to- Cl_b interactions. When I first read the article, I wondered if the heterocubane was the crystal's main unit or the dimer $(\text{SeCl}_4)_2$. I then calculated the dimer at the same theoretical level used by Guzmán-Hernández & Jancik to determine if it is a stable structure in the gas phase or due to the crystal packing. The dimer resembles the diborane structure, with bridging atoms between two units, forming a four-membered ring, as shown in Fig. 1. The calculation shows that the dimer is stable, formed from two C_{2v} SeCl_4 molecules with a formation energy of $-10.58 \text{ kcal mol}^{-1}$, where the axial chlorides

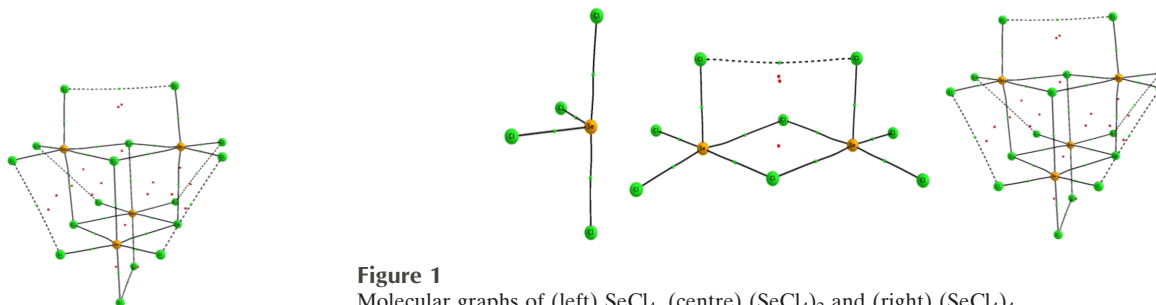


Figure 1
Molecular graphs of (left) SeCl_4 , (centre) $(\text{SeCl}_4)_2$ and (right) $(\text{SeCl}_4)_4$.

become the bridging atoms, increasing the electron population by 0.04 e. At the same time, the selenium decreases by 0.03 e. The selenium lone pairs are oriented outside the ring plane and do not have any role in the Se...Cl interactions. Once the dimer is formed, it is possible to stabilize the heterocubane structure from two dimers with an energy of around $-30.3 \text{ kcal mol}^{-1}$. The four lone pairs within this structure are oriented toward the centre of the cube.

The article by Guzmán-Hernández & Jancik (2024) is an excellent example of how QC-QCT methodology can extract structural information from a crystal.

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