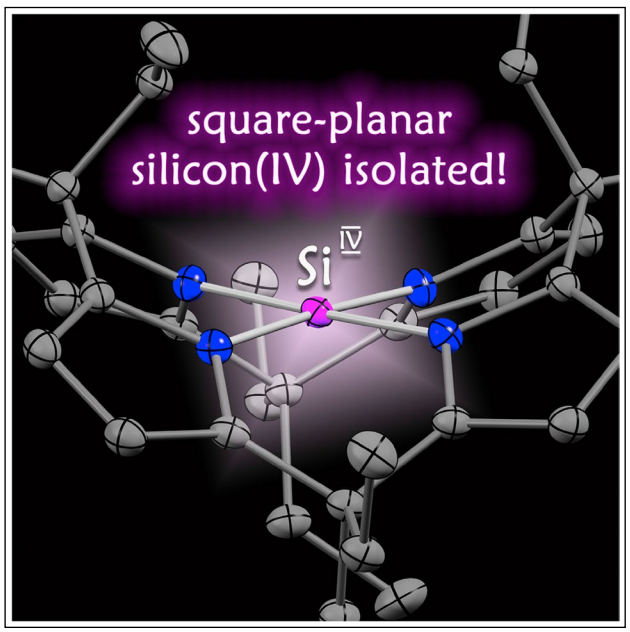
Square-planar silicon (IV) offers surprising properties

Fabian Ebner and Lutz Greb from Universität Heidelberg in Germany have isolated the first known square-planar silicon (IV) complex. They synthesized the compound, subjected it to several studies, and characterized it. They also performed computational studies to confirm the observed properties. Not only does this square-planar complex differ from other silicon-containing compounds in spatial arrangement, but it also shows outstanding properties, as reported in a recent issue of *Chem* (https://doi.org/10.1016/j.chempr.2021.05.002).

The researchers say that this new flattened structure *provokes* a range of features that enable new applications in catalysis and materials science. Using a nitrogen-containing pyrrole macrocycle (calix[4]pyrrolato) coordinated to a central silicon (IV) atom was crucial to stabilize the structure. The researchers also found a new characteristic frontier orbital arrangement; the complex has a small HOMO/LUMO gap that enables bond activation (where HOMO is the highest occupied molecular orbital and LUMO is the lowest unoccupied molecular orbital).



First-known isolated square-planar silicon (IV) complex. Credit: *Chem*.

The researchers grew single crystals from the complex, and subjected them to single-crystal x-ray diffraction analysis (SCXRD). The results showed typical Si–N bond lengths, and the planarity of the structure was confirmed by an almost ideal square-planar coordination geometry with angles of 178.2° and 176.1° for N–Si–N in opposite corners, and 90.2° for N–Si–N in adjacent corners. In addition, the SCXRD results showed a peculiar interaction between CH_2 groups from the ligands and the central silicon (IV) atom. Two methylene groups are oriented toward the central atom yet the C–H···Si lengths differ by almost 40 pm. This finding is characteristic of an attractive interaction between these atoms, which is common for C–H agostic (ligand–metal) interactions in transition metal complexes.

One of the other outstanding features is the modification of the frontier orbitals. The LUMO is lowered in comparison to the silicon tetrahedral geometry and is localized at the silicon. This explains the electron uptake in redox studies also reported in the article. In contrast, the HOMO is raised in comparison to the silicon tetrahedral geometry and localized in the ligand's π system. This small energy gap explains the square-planar complex's light absorption in the visible region, something that does not happen for the tetrahedral geometry complex. Another property that is enhanced by this energy gap is bond activation, which the researchers confirmed by subjecting the complex to reactions.

Hence, by isolating the square-planar silicon (IV) complex and characterizing it, the research team has gained new information about silicon and its chemistry. New redox chemistry behavior, ligand–metal interactions, visible light absorption, and reactivity are all explored and rationalized, which they expect will lead to applications in catalysis, photochemistry, and materials science.

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