Hypervalency – Experimental Charge Density Uncovers a False Concept

Dietmar Stalke[a], Dirk Leusser[a], Niko Kocher[a], Julian Henn[a], [a]*Institut. für Anorganische Chemie, Am Hubland, 97074 Würzburg, Germany.* E-mail: dstalke@chemie.uni-wuerzburg.de

Recently we synthesised and experimentally determined the charge density in molecular species containing so-called hypervalent central atoms. In those compounds formally the amount of valence electrons at the central atom exceeds the number of eight. Typical text book examples are SiF_6^{2-}, PF_6 or SO_3. Historically 3d orbitals are employed to explain the valence expansion and the generate sp^3d or sp^3d^2-hybrid-orbitals. However, the promotion of a phosphorus 3p electron to the d-orbital 16 eV are required but only 1 to 5 eV received by each covalent bond. Theoretical chemistry uncovered hypervalency as a false concept long time ago.[1] We investigated the phenomenon in terms of experimental charge density and topological analysis[2] of the hexacoordinated silicon complex $[F_2Si\{O(Me_2NN)\ CPh\}_2]$, the lithiumiminophosphoranate $[(Et_2O)Li\{Ph_2P(CHPy)(NSiMe_3)\}]$, and the sulfur triimide $S(N^tBu)_3$.[3]

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