Bruker / MIT Symposium 2019

BASIC CHEMICAL CONCEPTS CHALLENGED BY EXPERIMENTAL CHARGE DENSITY

Dietmar Stalke, Universität Göttingen, e-mail: dstalke@chemie.uni-goettingen.de

From the knowledge of the distances at the atomic level and the arrangement in the solid phase many properties, both at the molecular and macroscopic scale, can be deduced. However, the most basic concept, the chemical bond and reactivity, is still vigorously discussed. Still there is room for interpretation, because single crystal structural analyses based on the independent atom model only provides the positions of the centroids of the atoms and the distances between the atoms. In the electron density maps there are no lines or dashes defining or even indicating the chemical bond and the nature of the bonding remains a matter of interpretation based on a bonding model. Hence the anecdote that a bond is where the chemist draws the line remains valid to a certain extent. Most of our understanding of the chemical bond is still deduced from the distances and angles, which are determined as a result of the crystallographic analysis and reactivity is introduced on this basis.[1]

Various topics are addressed in the talk and connected to reactivity:

1) Lone pair regions are as important to study as the bonding region, demonstrated especially in low-valent silicon and phosphorus chemistry.[2,3]
2) Hypervalency can be ruled out for the sulfate dianion from charge density investigations.[4]
3) Lithium amide bonds are on par with lithium amine bonds, hence the latter are central to steer reactivity.[5]

References

[1] Review: Stalke, D. (**2016**). *Struct. Bonding*, **169**, 57-88.
[2] Niepötter, B., Herbst-Irmer, R., Kratzert, D., Samuel, P. P., Mondal, K. C., Roesky, H. W., Jerabek, P., Frenking, G., Stalke, D. (**2014**). *Angew. Chem. Int. Ed.*, **53**, 2766-2770.
[3] Henn, J., Meindl, K., Oechsner, A., Schwab, G., Koritsanszky, T., Stalke, D. (**2010**). *Angew. Chem. Int. Ed.*, **49**, 2422-2426.
[4] Schmøkel, M. S., Cenedese, S., Overgaard, J., Jørgensen, M. R. V., Chen, Y.-S., Gatti, C., Stalke, D., Iversen, B. B. (**2012**). *Inorg. Chem.*, **51**, 8607-8616.
[5] Engelhardt, F., Maaß, C., Andrada, D. M., Mata, R. A., Herbst-Irmer, R., Stalke, D. (**2018**). *Chem. Sci.*, **9**, 3111-3121.