Charge Density Measurements of Orthorhombic Sulfur

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Our goal in this project is to establish experimental charge density studies as a routine method in our facility. Our group is interested in the elucidation of weak interactions, as can be found in weakly bound Lewis-Acid-Lewis-Base complexes, non-classical carbonyl complexes or ionic liquids. Such interactions are often strongly influenced by dispersion, which complicates their quantum chemical treatment. In order to describe bonding in these complexes properly, highly accurate methods must be employed. Experimental charge densities can support and supplement our theoretical studies in these fields. On the synthetic side, we use *weakly coordinating anions* (WCAs) to simulate *pseudo gas phase conditions* in the solid state, which allows us to obtain charged complexes which are almost undisturbed by Coulombic interactions.[1]

One such class of compounds we plan to examine are cationic complexes $[M(S_n)_x]^+$ with M = Cu, Ag, n = 8, 12 and n = 1, 2 (and related systems with e.g. P_4 or P_4S_3 ligands).[2] However, for several reasons these compounds are not suitable for learning and practicing the method: The cells are quite large and often the crystallographic symmetry is low. Twinning is quite common. Also, usually the crystals have to be mounted under inert conditions at low temperatures, often with negative effects on the crystal quality. In search for an easy-to-handle alternative we found that although Coppens et al. have reported charge density measurements of orthorhombic sulfur at 100K already in 1977 (κ model),[3] to our knowledge no multipolar refinement has been reported yet.

Therefore, orthorhombic S_8 was a logical first choice. It reproducibly forms well-defined, well-scattering, air- and moisture-stable crystals (which refine to very low R values), obviously contains no heavy atoms, has been thoroughly studied theoretically and knowledge of its charge distribution may facilitate subsequent studies of the more demanding Cu- and Ag-S_8 complexes.

High-quality high-angle data were recorded and refined using a multipolar model, showing that the necessary data quality can be obtained on our home Xray equipment. Topological analyses and accompanying quantum chemical calculations are currently in progress.

Literature:

[1] I. Krossing, I. Raabe, *Angew. Chem. Int. Ed.* **2004**, *43(16)*, 2066. [2] T. S. Cameron, A. Decken, I. Dionne, M. Fang, I. Krossing, J. Passmore, *Chem. Eur. J.* **2002**, *8*, 3386; I. Krossing, *J. Am. Chem. Soc.* **2001**, *123*, 4603; I. Krossing, L. Van Wüllen, *Chem. Eur. J.* **2002**, *8*, 700; I. Krossing, A. Reisinger, *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 5725. [3] P. Coppens, Y. W. Yang, R. H. Blessing, W. F. Cooper, F. K. Larsen, *J. Am. Chem. Soc.* **1977**, *99(3)*, 760.