Oral presentation

Improved Modelling of 3D ED Data for Studying Charge Distribution of Iron(III) Acetyl Acetonate

Laura Pacoste

Stockholm University
laura.pacoste@mmk.su.se

In this study, we examined the charge distribution in an organometallic complex using three-dimensional electron diffraction (3D ED), with a focus on modelling charged species like iron. We refined structural model of a metal-organic complex called iron(III) acetylacetonate (FeAcAc), using both the Independent Atom Model (IAM) and the Transferable Aspherical Atom Model (TAAM). TAAM refinement initially employed multipolar parameters from the MATTS databank for acetylacetonate, while iron was modeled with spherical and neutral approach (TAAM-ligand). Later, custom TAAM scattering factors for Fe-O coordination were derived from DFT calculations (TAAM-ligand-FeIII). Our results show that IAM, when assigning charges corresponding to the iron's oxidation state, inaccurately represents electrostatic potential maps and overestimates the scattering power of the iron. In contrast, TAAM significantly improved the model accuracy, evidenced by improved R1 values, goodness-of-fit (GooF) and reduced noise in the Fourier difference map. For 3D ED, R1 values improved from 19.36% (IAM) to 17.44% (TAAM-ligand) and 17.49% (TAAM-ligand-FeIII), and for single-crystal X-ray diffraction (SCXRD), from 3.82% to 2.03% and 1.98%, respectively. For 3D ED, the most significant R1 reductions occurred in the low-resolution region (8.65-2.00Å), dropping from 20.19% (IAM) to 14.67% and 14.89% for TAAM-ligand and TAAM-ligand-FeIII, with less improvement in high-resolution areas (2.00-0.85Å). This indicates that the major enhancements are due to better scattering modeling in low-resolution zones, benefiting larger structures like metal-organic frameworks (MOFs) and proteins. Furthermore, our analysis highlights the more crucial role of organic ligands in charge distribution, with asphericity mainly within these components. Bader charge analysis further confirmed that the iron charge is smaller than its formal oxidation state. This study provides new insights into refinement of charge distribution in FeAcAc against 3D ED data, suggesting the need for more accurate modeling methods and highlighting the potential of TAAM in examining charge distribution of large molecular structures such as MOFs and proteins using 3D ED.