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Enhanced Structural Insights: Evaluating Hirshfeld Atom Refinement versus Independent Atom Modelling in Pentacoordinate Sn(IV) Complex

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The Hirshfeld atom refinement (HAR) is a sophisticated method used in crystallography to obtain highly accurate and precise model of the electron density distributions within molecular crystals. This approach refines the positions of atoms in a crystal structure by using quantum mechanical calculations of aspherical atomic scattering factors through the use of Hirshfeld stockholder partitioning [1]. HAR offers advantages over the traditional Independent Atom Model (IAM) providing a better fit of experimental data, often in good agreement with those obtained from neutron diffraction and multipole refinement, which are considered more accurate methods [2,3]. HAR improvements in accuracy and precision of electron density models can reveal subtle features of chemical bonding as well as a more detailed understanding of the intermolecular interactions.
As an application we compare here the results from IAM and HAR methodologies of the pentacoordinate complex [$SnClMe_2(L)$], where L = 4-(dimethylamino)benzaldehydenicotinic hydrazone. The metal center coordinated to one chloride and two methyl ligands, along with one hydrazonate ligand. This hydrazonate ligand functions as a bidentate ligand, attaching to the Sn(IV) through an N,O chelating system and existing as the Z isomer around the iminic bond. Comparing the two refinement methods, HAR showed superior statistical parameters (R1 = 1.87%, wR2 = 3.66%) compared to IAM (R1 = 2.30%, wR2 = 5.19%). This higher precision is further emphasized by the cleaner residual density map produced by HAR (Figure 1).

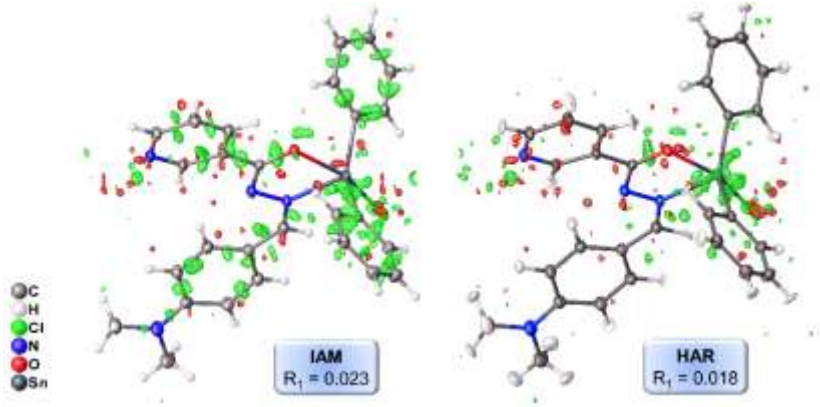

Figure 1. Residual density maps using IAM (left) and HAR (right) methods for [SnClMe2(L)]. Green and red contours are positive and negative, respectively.

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