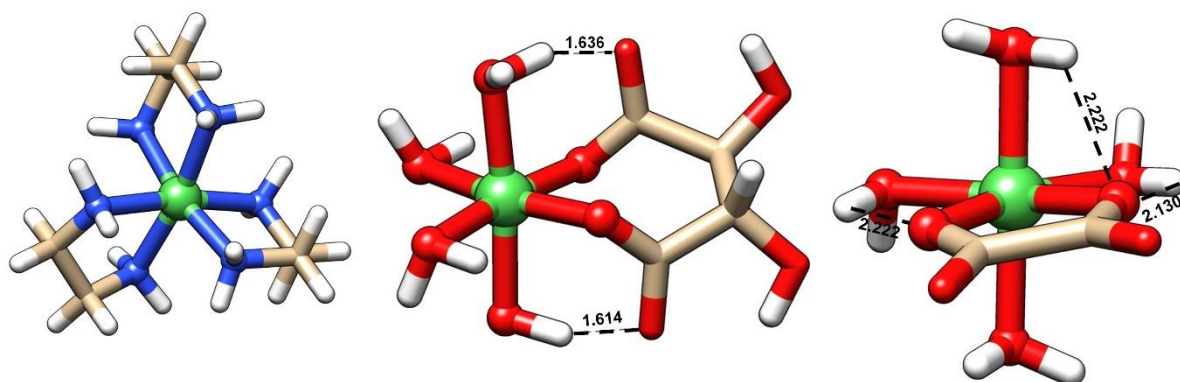


# Synthesis of Ligand-Stabilized NiSe Nanostructures: Thermodynamic effects of Intermediates

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A ligand-mediated room temperature synthesis route is reported for the preparation of NiSe in the pure phase. The synthesis involved carboxylic acid-based ligands and elemental Se as selenide source to facilitate the synthesis. The role of functional groups in ligands are probed by synthesizing NiSe materials by varying the ligands that have different functional groups. The presence of dicarboxylic acid groups in the ligand played a key role in the synthesis of nickel selenides. In particular, the oxalate and tartrate complexes of nickel were conducive pathways towards the formation of nickel selenide crystals. On the other hand, the ethylene diamine complex with Ni(II) yielded an amorphous slurry when reacting with the selenide precursor. The computations aimed to explain the difference on why certain complexes of Ni(II) worked as a desired pathway to form nickel selenide crystals while other complexes did not.



**Figure 1.** Optimized geometries at the B3LYP/def2-TZVP level, of the nickel complexes with (L-R) ethylene diamine(EN), tartaric acid (TAR) and oxalic acid (OXAL).

The computations optimized the stable geometries and geometric parameters of the nickel complexes with TAR, OXAL and EN ligands. Binding energy calculations under experimental conditions reveal the higher likelihood of the carboxylate complexes to form crystalline NiSe as compared to the  $[\text{Ni}(\text{EN})_3]^{2+}$  complex at room temperature. The importance of entropic effects is discussed and the formation of the crystals from the  $[\text{Ni}(\text{EN})_3]^{2+}$  complex is predicted at high temperatures. This prediction has been validated by experimental findings.