Nuclear Quadrupole Interactions in Cadmium Complexes: Semiempirical and *ab initio* Calculations

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Semiempirical calculations, based on the so-called angular overlap model, have been compared with *ab initio* methods (MP2) for the calculation of nuclear quadrupole interactions (NQI's) in cadmium complexes with biologically relevant ligands (H_2O, OH^-, cysteinate, carboxylate, and imidazole). The assumptions on which the semiempirical model is based have been tested and the comparison indicates that: 1) A change in the Cd–ligand bond length by 0.1Å may change the electric field gradient (EFG) by about 0.2 a. u.. A simple scheme to incorporate such effects in the semiempirical method is suggested. 2) The effect of ligand–ligand interactions is up to about 0.2 a. u. for the largest diagonal element of the EFG tensor for the tested complexes, and such effects can significantly influence the so-called asymmetry parameter. 3) The position of non-coordinating atoms on the ligands can in some cases (e. g. the hydrogen atoms of water) significantly influence the EFG. The combined effect of non-coordinating atoms and ligand–ligand interactions may cause deviations of up to 0.35 a. u. between *ab initio* and the semiempirical calculations. 4) In the semiempirical model each ligand is characterised by one parameter, the so-called partial nuclear quadrupole interaction. This parameter has been evaluated by *ab initio* calculations, and agreement was found within about 0.2 a. u. (≈ 40 Mrad/s) for all ligands except imidazole. 5) A change in the coordination number from 2 to 6 may change the partial NQI by about 0.3 a. u.

Key words: Electric Field Gradient; Angular Overlap Model; Ligand Additivity.