INOR 823 Theoretical investigations of supramolecular chemisorption adducts of volatile small molecules with a trinuclear silver(I) nitrated pyrazolate complex: DFT modeling of dipole-quadrupole interactions

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A comparative study on the tendency of a new trinuclear silver(I) pyrazolate, namely [N,N-(3,5-dinitro-pyrazolate)Ag]$_3$ (1) and a similar compound known previously, [N,N-(3,5-bis(trifluoromethyl)pyrazolate)Ag]$_3$ (2) to adsorb small volatile molecules was performed. It was found that 1 has a remarkable tendency to form adducts, at room temperature and atmospheric pressure, with acetone, acetylacetone, ammonia, pyridine, acetonitrile, triethylamine, dimethylsulfide, and tetrahydrothiophene while CO, THF, alcohols, and diethyl ether were not adsorbed. On the contrary, 2 did not undergo adsorption of any of the aforementioned volatile molecules. Density Functional Theory (DFT) results (polarizability, electrostatic potential profiles, kinetics and thermodynamics, and positive point charge calculations) are consistent with the chemisorption model, explain the experimental adsorption selectivity for 1, and the lack of similar adsorption by 2 upon proper selection of the density functional. The M06 method in conjunction with CEP-31G basis set provides good agreement with the experimental data both qualitatively and quantitatively compared to B3LYP/CEP-31G. The results suggest that the adsorption of Lewis basic vapors occurs mainly by kinetic effects. The high vs. low binding energies calculated for the adducts of 1 with acetonitrile vs. CO manifest the experimental findings. The findings in this project suggest that this class of quadrupolar macromolecular complexes may exhibit potential for toxic industrial chemical (TIC) removal applications already known for porous organic polymers.