

Quantum-chemical studies of benzene-1,2-dithiolate complexes with Cu, Ni and Co

S. Šoralová and M. Breza

*Department of Physical Chemistry, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovakia
(e-mail: stanislava.soralova@stuba.sk, martin.breza@stuba.sk)*

Experimental studies show that the complexes of benzene-1,2-dithiolate (bdt) and of its derivatives with three different central atoms have MS_4 coordination sphere in very slightly distorted square-planar configuration. Some experimental studies indicate that central atoms M in all complexes are in oxidation state III.

This study is focused on the complexes of general formula $[M(bdt)_2]^q$, $q = -1, -2$ or -3 , $M = Cu, Ni, Co$. The geometries obtained from experimental measurements were optimized at B3LYP level of theory. Because 6-31G* basis set proved to be insufficient even for geometrical optimizations, all presented results are obtained using 6-311G* basis set.

The dependence of central atom oxidation state on the total charge and spin multiplicity of the complexes has been studied. The electron structure has been evaluated in the terms of Mulliken population analysis and QTAIM (Quantum Theory of Atoms-in-Molecules) topological analysis of the electron density. The oxidation state of central atoms has been determined according to the number of d -electrons.

The total energy of all complexes increases with increasing negative total charge of the complex likewise the strength of central atom-sulphur bonds weakens with increasing negative total charge. The oxidation state of all central atoms based on their d -electron populations varies slightly between I and II only. The ligands in all complexes are planar but their mutual position varies from coplanar to orthogonal.

In general, the stability of studied complexes decreases with increasing number of electrons in the complex as indicated by energies, bond lengths and bond critical point electron densities.