IIs06-009

DFT study of the [Ni(H2O)2(phen)(C4H2O4)2]2- coordination complex and Hirshfeld surface analysis of its intermolecular interactions in crystalline lattice

Viana, J.R.(1); Lima, A.D.S.G.(1); Dos Santos, A.O.(1); Carneiro, J.W.M.(2); Lage, M.R.(1);
(1) UFMA; (2) UFF;

Computational methods have been widely used to analyze structural arrangements in coordination chemistry. It is even more important in the study of complexes containing metal ions and with different sterically hindered ligands. Since DFT has been successfully used in the study of bonds formed between metal ions and bonding atoms of different ligands in coordination complexes, DFT calculations were performed for the study of geometric, electronic and thermodynamic properties of the [Ni(H2O)2(phen)(C4H2O4)2]2- complex. The calculations were done using the B3LYP DFT functional, with the G16 software. The 6-311++G(d,p) basis set was employed for the H, N, C and O atoms, and the SDD pseudopotential was used for the Ni atom. Solvation effects in a mix of solvents (water and methanol 1:1 v) were considered by using the PCM solvation method. A Hirshfeld surface analysis was also performed from the crystal structure data, with the aid of the Crystal Explorer 17 software. Surfaces were mapped as a function of normalized distance (dnorm) and plotted against 2-D fingerprints. The optimized geometry shows an octahedral arrangement of the ligands around the nickel atom, which is bonded to two N atoms of phenanthroline, O atoms of two maleate ions and two water molecules that close the coordination sphere. Thermodynamic properties of the systems were also calculated. Negative values were found for the enthalpy and Gibbs free energy changes upon coordination (Gibbs free energy variation = –84.50; enthalpy variation = –140.76 kcal/mol). The boundary molecular orbital orbitals were studied, which revealed that HOMO is mainly distributed over the maleate ion, while LUMO is mainly located on phenanthroline. HOMO energy is –6,17 eV and LUMO energy is –2,36 eV, respectively, with a calculated HOMO-LUMO gap of 3,81 eV. The 3D Hirshfeld surfaces showed the regions corresponding to the shortest contacts between atoms and the 2D fingerprints indicated that H...H and O...H interactions are the most expressive. The geometric parameters calculated for the complex are in a good agreement with experimental data and the thermodynamic data obtained indicate that the coordination is spontaneous and exothermic. The HOMO-LUMO gap suggests that the electronic structure of the complex is reasonably stable. The Hirshfeld surface analysis revealed the main regions of short interactions between atoms and the most significant interactions were quantified. Y. Q. Zheng, J. L. Lin, Z. P. Kong, B. Y. Chen, J. Chem. Crystallogr., v.32, p. 399, 2002. C. R.M.O. Matos, L. S. Vitorino, P. H.R. de Oliveira, M. C. B.V. de Souza, A. C. Cunha, et. al., J. Molec. Struc., v.1120, p. 333, 2016. A. Bouchoucha, A. Terbouche, A. Bourouina, S. Djebbar, Inorg. Chim. Acta, v. 418, p. 187, 2014.