

## Theoretical study of cis and trans structures [Zn(dmso)<sub>2</sub> (H<sub>2</sub>O) (fum)], where dmso = dimethylsulfoxide fum = fumaric acid

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**Abstract:** The large number of compounds that may exhibit cis-trans isomerism in inorganic chemistry illustrates, in terms of number of known examples, the progress of synthetic inorganic chemistry. In fact, from the studies conducted by Werner at the beginning of this century to the present day, a huge range of works involving this type of isomers can be found in the literature.<sup>1-7</sup> In the case of isomers in inorganic complexes it is always important to remember that their synthesis, proof of their molecular structures and an evaluation of their properties, provide the decisive arguments for Werner to develop and defend his own theory of coordination<sup>8-13</sup>. The calculations were performed using the Gaussian 98W computational software.<sup>28</sup>

The equilibrium geometry of the studied molecules were calculated using as base set of functions: 6-311 ++ G (3df, 3pd) in the mode DFT B<sub>3</sub>LYP.

The first step of the work consisted in minimizing the molecular energies of the equilibrium geometries for the cis and trans structures, assuming the presence of two water molecules of hydration as observed experimentally in the case of the trans isomer by X-ray diffraction. Such geometries are shown in Fig.1 As expected, due to the presence of water and consequent hydrogen bonds, the "Trans" structure presents a lower energy The most abundant under normal experimental conditions. There is also an unacceptable deformation of the octahedral coordination of Zn in the cis structure due to the van der Waals repulsion between the sulfoxides groups.

The calculated energies with a variation of 2.4 Kcal / mol being a more stable trans structure in the cis structure as binding distances calculated in the Zn-O coordination range from 1.86 to 1.88 Å and the angles calculated in the coordinates range from 104, 96 to 148,85 °, demonstrating a shortening in the bonds, proving a distortion of the octahedral in this conformer. As calculated distances and angles for the trans structure are according to a literature found for the same conformer.

Taking into account these results, we performed calculations of energy minimization of the structures, taking as hydration water the coordination of zinc, for analysis of geometric change related to the position of ligands in cis or trans.

It can be observed that the cis binder generates a tetrahedral geometry with coordinating angles between 108.64 ° and 110.66 °, whereas for the ligands in trans a geometry is presented a planar square where the coordination angle varies between 90.35 ° And 89.75 °.



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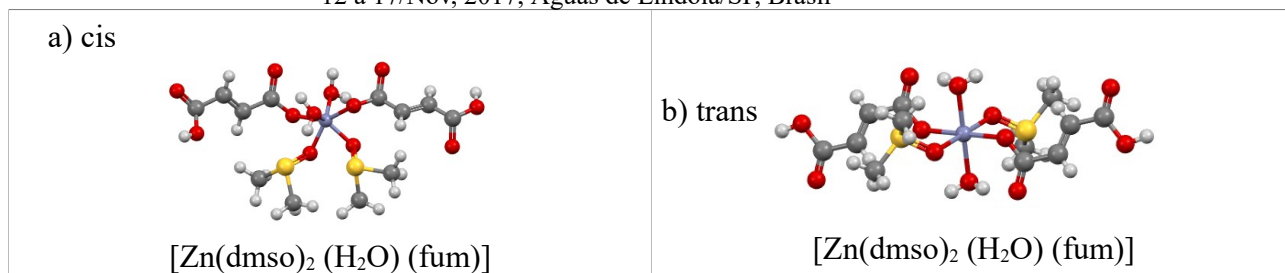


Figure 1. Optimized geometries in the DFT calculation of confounders "Cis" and "Trans"

Already the energy of these structures are closer together varying only 0.1 kcal / mol, where the cis structure has an energy of 2.4 kcal / mol and the trans structure has an energy of 2.3 kcal / mol, thus demonstrating , That the trans structure remains more stable than cis, but the two structures now can coexist.

When calculations were carried out, hydrating the tetracoordinate molecules, both cis and trans structures, resulted in a hexaco-ordinate structure with octahedral geometry and energy close to an initially isolated structure (E = -2.1 Kcal / Mol).

Analyzing the results obtained by the theoretical calculations, it can be observed that the octahedron of the coordination of the zinc, this distorted in cis, for a good repulsion of spills between the sulfoxides groups. When the coordination of zinc to tetracoordinate is changed, a cis structure has a tetrahedral geometry and a square trans square. As the energies are calculated for the two indicative structures, they can be found, since the energy difference between a cis and trans is small.

But next to the tetracoordinated cis complex a convergent structure for a hexacoordinate transaction with a calculated isolated molecule energy, thus concluding that a hexacoordinated cis structure with 4 ligands and 2 waters is experimentally unlikely.

**Key-words:** Theoretical calculations, geometric isomerism, energy, stability

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