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Theoretical investigation of polymer chain stability in the metal coordinated azorubine and cyclam complex

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ABSTRACT

Theoretical investigations have been performed for *unit* systems with Ni(II) and Zn(II) coordination between azorubine and 1,4,8,11-tetraazacyclotetradecane (cyclam) complexes using the conventional DFT and the DFT-based tight binding (DFTB) methods. Two different geometries (*short* and *long*) and spin states (*singlet* and *triplet*) of the *model* system built by two mesylate groups and the cyclam ring together with Ni(II) and Zn(II) ions were energetically characterized. For the Ni(II) coordination complex the triplet geometry is preferred, but one could not exclude also the presence of the singlet spin configuration due to the huge energy barrier defined by the intersystem crossing. The intersystem crossing geometry of the singlet–triplet transition was studied in details and the corresponding spin–orbit couplings were discussed. For the Zn(II) coordination complex only the singlet state was found. Polymer chain build up from four *unit* systems presents irregular forms with strong coordination bonds between units.

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1. Introduction

In the field of coordination polymer/metal organic frameworks research, networks based on sulfonic organic compounds are less common due to the weak coordination force [1–3] of the sulfonate anion. On the other hand, weaker ligand forces combined with large numbers of coordination modes would have a great advantage because it makes possible higher crystal packing flexibility, a very important property for coordination polymer chemistry [4–6]. Spherical shape of the sulfonate group makes a priori the coordination a challenge, although it appears as monoanions (RSO_3^{-1}). This lack of regular inorganic assembles without a well-defined directionality is not completely detrimental because the new inorganic cluster can be formed in situ and the structure-directing role of the organic linker can be enhanced. In contrast to other materials, sulfonate coordination polymers offer a greater chance to form polar pores [7]. The spherical ligating ability of the sulfonate group makes easier the coordination in three dimensions. There are a few studies on supramolecular motifs of various sulfonated azo dyes [8–12]. One difficulty in examining sulfonated dyes is that they exhibit generally poor crystal growth properties, making single crystal diffraction studies difficult. The utilization of macrocyclic complexes offers several advantages over free metal ions in the assembly of multidimensional coordination polymer networks. For example, these complexes enable the control of the extending direction of networks, which simplify the network structures [13–18]. For preparation of sulfonated coordination polymers, metal–macrocyclic complexes were seldom used, only eight compounds [1,2,19–23] being known till now.

The presence of a transition metal atom at the center of the molecule enhances spin–orbit coupling, leading to a marked activation of intersystem crossing from singlet to triplet manifolds. Thus, knowledge of location of triplet excited electronic states is important for understanding the lack of fluorescence in different metal–ligand complexes like metalloporphyrins [24]. This magnetic bistability was experimentally observed even at room temperature [25]. Several theoretical studies attempted to explain the electronic absorption spectrum of such metal–ligand molecular complexes. Patchkovskii et al. [26] have shown that in case of nickel–porphyrin complexes a small singlet–triplet energy gap can be observed, and they propose a new mechanism for the decay of optically active excited states into this triplet manifold. Similar conclusions were drawn by Carrasco et al. [27] in case of Ni and N′-methyloxamidate complex and by Bachler et al. [28] for nickel complexes containing two o-semiquinonato type ligands. Based on these theoretical works one can conclude that in case of the nickel(II) transition metal ion an energetically favorable

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singlet–triplet transition can occur due to the small energy gap between the spin states.

Cyclams – fourteen-membered tetraamine macrocycles – also show the ability to complex various transition metal cations and their complexes are often highly thermodynamically and kinetically stable with respect to metal ion dissociation [29]. Füzerová and coworkers [30] have demonstrated experimentally that the ligand between the cyclam ring and cooper(II) ion forms a very stable complex, with a high selectivity over binding of other metal ions, like Zn(II), Mn(II), Cd(II), etc.

The goal of our theoretical investigation is to give a detailed description of the stability of azorubine system coordinated with Ni(II) and Zn(II) ions inserted in the cyclam macrocycle. We also study the stability of azorubine polymer (oligomer) chains built by up to four molecular units in the same environment.

2. Computational details

Equilibrium geometries of different molecular complexes with singlet or triplet spin states have been optimized at DFT level of theory using the M11 [31] exchange–correlation (XC) functional and def2-TZVP [32] basis set implemented in the Gaussian09 program package [33]. The M11 XC functional employs dual-range exchange to provide good accuracy for molecular systems with single-configurational or multi-configurational characters, and to describe well barrier heights of chemical reactions and charge transfer effects. It was proved that the functional has also good performance for describing Rydberg as well as valence states in the framework of the adiabatic time-dependent density functional theory [34]. On the other hand, the BSSE effects were not considered as by construction the M11 XC functional was parameterized to cover these effects. The global or local minima of different molecular geometries were obtained considering the Berny geometry optimization algorithm [35] in redundant internal coordinates implemented in the same Gaussian09 program package. The default optimization convergence criterion of 10^{-8} a.u. in the energy was considered for each optimization case. The charge distribution and the Wiberg's bond-order index analyses were performed considering the natural population analysis (NPA) [36–38] through the NBO module built in the Gaussian09 package. Afterward, in order to study the polymer (oligomer) properties, at least 3–4 molecular units have been included in our geometry structure. These structures usually contain a large number of atoms (over 200 atoms) which could not be properly studied with the conventional *ab initio* or DFT methods, due to the huge computer capacity requirement. The density functional-based tight binding method combined with the self-consistent charge technique (SCC-DFTB) [39] can be considered as an adequate solution for treating large biological or nano-scaled molecular materials with an accuracy closed to the case of high level theoretical methods [40–43]. The large system built up by four units was investigated using the DFTB+ [44,45] program based on the SCC-DFTB technique. The appropriate sets of atomic parameters were taken from the corresponding *mio* [39,46] and *znorg* [47] sets of Slater–Koster files. Molecular structures were visualized and analyzed using the Gabedit [48] molecular graphics program, whereas the molecular graphics (figures) were created using the Avogadro [49] software. The intersystem crossing point search was performed using a homemade routine based on the "Penalty function" algorithm proposed by Ciminelli et al. [50] and choosing similar optimization parameters as it was proposed by Keal et al. [51]. The "Penalty Function" by construction minimizes the average of the two states energies without altering the position of the minimum of the crossing point [50]. The only condition is that the geometry of the lowest energy state should be taken as the starting geometry for the minimization procedure. The corresponding energy values and energy gradients for each optimization step were obtained using again the Gaussian09 program package. For the calculation of the spin–orbit coupling between the singlet and triplet states in the geometry configuration of the intersystem crossing point the MolSOC software [52,53] has been used.

3. Results

3.1. Ni(II)–cyclam complex

The molecular structure of the unit system is built by two Ni(II)–1,4,8,11-tetraazacyclotetradecane rings bound to the two mesylate groups of azorubine. For its geometry see Fig. 1. In order to draw a more clear picture about the coordination complex of dimesylate–Ni(II)–1,4,8,11-tetraazacyclotetradecane we have investigated its electronic configuration in more detail. The 1,4,8,11-tetraazacyclotetradecane (cyclam) is a cyclic chemical ring that consist in the alternating connection of two $-(CH_2)_2-NH-$(ethylamine) and two $-(CH_2)_3-NH-$(propylamine) sequences. The Ni(II) square-planar coordination complex is presented in Fig. 2. Two more coordination bonds can be formed between the Ni(II) and the oxygen anions of the mesylate groups and finally one obtains the octahedral six-coordination mesylate–Ni(II)–cyclam metal–ligand complex, called as the *model* system henceforth. The two S = O double bonded oxygen atoms from each mesylate fragment can act as electron donors and can form hydrogen bonds (H-bond) with the N–H groups of cyclam. When two N–H groups are oriented towards the same mesylate fragment we denote by "*short*" the configuration when the two N–H groups are connected by an ethylamine chain and by "*long*" the configuration when a propylamine chain is in between (see Fig. 3).

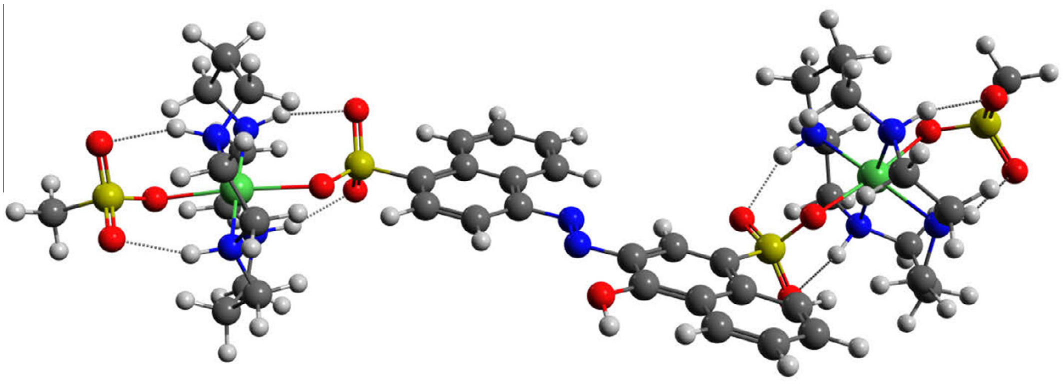

Fig. 1. The geometry structure of the dimesylate–Ni(II)–1,4,8,11-tetraazacyclotetradecane complex.

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