DFT STUDIES ON THE TETRANUCLEAR CUBANE
COMPLEX $[\text{Ni}_4(\text{ampd})_4(\text{Cl}_4)] \cdot \text{MeCN}$

G. Abbas,1 Mariya-al-Rashida,2 A. Irfan,3 U. Ali Rana,4 and I. Shakir4

Density functional theory (DFT) is used to investigate the structural properties of Ni(II) cubane $[\text{Ni}_4(\text{ampdH})_4\text{Cl}_4]\cdot\text{MeCN}$. The structural features and ground state geometry calculations are computed at the B3LYP/6-31G* (LANL2DZ) level of theory. We shed light on the highest occupied molecular orbital and lowest unoccupied molecular orbital. The absorption spectrum is calculated using time-dependent DFT. The absorption wavelengths are calculated using different functionals, i.e., pw91pw91, B3LYP, BHandHLYP, CAM-B3LYP, LC-BLYP, and M06. The LC-BLYP is in good agreement with the experimental data.

DOI: 10.1134/S0022476614010053

Keywords: Ni(II) cubane, 2-amino-2-methyl-2,3-propanediol, single crystal X-ray crystallography, density functional theory, time-dependent density functional theory.

INTRODUCTION

The synthesis of polynuclear metal complexes has attracted immense interest in the last two decades [1]. The high nuclearity nickel aggregates possess aesthetically pleasing structures and are also relevant to many important fields, including bioinorganic chemistry and molecular magnetic materials. In the former field, the synthesis and characterization of nickel(II) hydroxo-bridged dimers is important since such species provide useful bioinorganic models for the intermediates in the catalytic mechanism of the metalloenzyme urease [2]. Similar clusters have sparked interest among scientists for their potential applications as biomimetic agents to study the enzyme catalysis [3-6]. More pronounced applications of polynuclear clusters of paramagnetic metals include their role as single molecule magnets (SMMs). The last decade has seen an explosion in the field of SMM research. One of the earliest molecules to be identified as SMMs were manganese oxide based clusters [7], however, many more iron [8], cobalt [9], and nickel [10] based SMMs have since been developed. What makes these molecules even more interesting is the phenomena of magnetic hysteresis, a property that offers much hope for the application of these materials as storage devices or qubits (quantum bits), providing impetus to push research in the direction of spintronics (spin based molecular electronic devices) [11]. Such materials are also strong candidates for the use in cooling applications owing to the presence of the enhanced magnetocaloric effect (MCE) [12].
Scheme 1. Structure of the ampdH$_2$ ligand

Fig. 1. Molecular structure of tetranuclear Ni(II) cubane [Ni$_4$(ampdH)$_4$Cl$_4$]·MeCN with solvent molecules removed. Some hydrogen atoms are omitted.

The first nickel based SMM was a cyclic dodecanuclear complex [13]. One successful synthetic methodology towards new Ni$^{II}$ compounds includes the employment of ligands that contain RO-groups since they have a high bridging capability, thus leading to polynuclear compounds and often propagating ferromagnetic interactions between the metal centers [11]. Some of the more commonly investigated RO-containing ligands include hmph (2-hydroxymethylpyridine), thmeH$_3$ (1,1,1-tris(hydroxymethyl)ethane), pdmH$_2$ (pyridine-2,6-dimethanol) and metheidiH$_3$ (N-(1-hydroxymethylethyl)iminodiacetic acid) [11]. We have already reported di- and tetranuclear lanthanide complexes obtained with the use of N-methyldeethanolamine and 2-amino-2-methyl-1,3-propandiol [14]. Few polynuclear complexes from this ligand have been reported to date, including a ferromagnetic decametallic mixed valent Mn supertetrahedron [15, 16], a mixed valent cobalt cluster [17], multinuclear Fe [18], Ni, and Co complexes [19]. Herein we report the DFT studies of a Ni cubane-like complex having the formula [Ni$_4$(ampdH)$_4$Cl$_4$]·MeCN, which we prepared with minor modifications of the already known method [19]. The crystal structure of the compound has been determined with single crystal X-ray crystallography (Fig. 1). These crystal coordinates were then used to define the initial atomic coordinates in the computational analysis. Using DFT and time-dependent DFT, we have shed light on the geometries, electronic and optical properties respectively.

EXPERIMENTAL

General and physical measurements. All chemicals and solvents used for the synthesis were obtained from commercial sources and were used as received, without further purification. The reaction was carried out under aerobic conditions. The compound was characterised by elemental analysis (CHN) using an Elementar Vario EL analyzer. Fourier transform IR spectra were measured on a Perkin-Elmer Spectrum.

Preparation of [Ni$_4$(ampdH)$_4$Cl$_4$]·MeCN (1·MeCN). A solution of 2-amino-2-methyl-1,3-propanediol ampdH$_2$ (0.079 g, 0.75 mmol) in MeCN (15 ml) was added dropwise over 20 min to a stirred solution of NiCl$_2$·6H$_2$O (0.119 g, 0.5 mmol) in MeOH (15 ml). The resulting mixture was stirred at room temperature (RT) for 2 h, filtered, and allowed to stand undisturbed in a sealed vial. Green coloured rods suitable for the single crystal X-ray diffraction analysis were obtained after 3 weeks.