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Theoretical study of bis(N-(5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-yl) ethanimidamidato)M complexes (M = Co, Ni, Cu, Zn, Pd, Cd): Structural, electronic and optical properties

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ABSTRACT

We present a theoretical study of the structure and electronic and optical properties of several L_2–M compounds where L is bis(N-(5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-yl)ethanimidamidato, or $C_{11}H_{11}N_4O_2$, and M = Co, Ni, Cu, Zn, Pd, Cd. Our calculations are carried out in the framework of the density-functional theory (DFT) using several families of density functionals, namely semi-local functionals, global hybrids and range-separated hybrids. Our results reproduce well the experimental data concerning the structure of the recently synthetized L_2–Cu compound. We also present the infrared spectra and absorption spectra in the visible–UV domain. The changes induced by the substitution of the Cu atom by another metal atom are investigated.

1. Introduction

Oxadiazoles constitute an important class of ligands in coordination chemistry due to their use in the synthesis of transition metal complexes. Such complexes have been demonstrated to bear important biological activities such as antibacterial [1,2], antimycobacterial [3], antifungal [4,5], anti-inflammatory [6,7], analgesic [8] and anticonvulsant [9,10]. There are three known isomers: 1,2,4-oxadiazole, 1,3,4-oxadiazole and 1,2,5-oxadiazole. However, 1,3,4-oxadiazole and 1,2,4-oxadiazole are better known, and more widely studied by researchers because of their many important chemical and biological properties [11]. Oxadiazole based ligands have been used for complexation metals, such as platinum, silver, palladium and copper [12–13]. The copper complexes with oxadiazol based ligands are important functional units in bioinorganic chemistry [14]. Copper is an essential trace element that is widely distributed in animal and plant tissues [15,16]. It also acts as a cofactor for a number of metalloenzymes such as catalase, peroxidase, cytochrome oxidase [17,18]. The substantial importance of copper in the biological systems has increased the interest in the coordination chemistry of copper with N, O donor ligands as biomimetic systems [19].

Recently, the compound bis(N-(5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-yl)ethanimidamidato)Cu, or $(C_{11}H_{11}N_4O_2)_2$–Cu, was prepared by solvothermal synthesis using 2-amino-5-(4-methoxyphenyl)-1,3,4-oxadiazole and copper sulfate pentahydrate in an acetonitrile solution [20]. Its structure has been determined from X-ray crystallography. The Cu(II) atom lies on an inversion center and is four-coordinated in a quasi-planar structure by four N atoms of the ligands obtained from the formation of a bond between the amine N atom of the oxadiazole molecule and the nitrile C atom of the solvent (Fig. 1).

In the present paper, we investigate both the electronic and optical properties of this copper complex, and also the changes in the properties when Cu is substituted by another metal. Our theoretical investigations are carried out in the framework of the density-functional theory (DFT) using several families of density functionals. Details of the calculations are given in the following section. In Section 3, we present and discuss our results concerning the structural parameters of L_2–M compounds where L = $(C_{11}H_{11}N_4O_2)$ and M = Co, Ni, Cu, Zn, Pd, Cd, and the electronic and optical properties.

2. Computational details

The geometrical optimization were performed in the framework of the density functional theory (DFT) using several density

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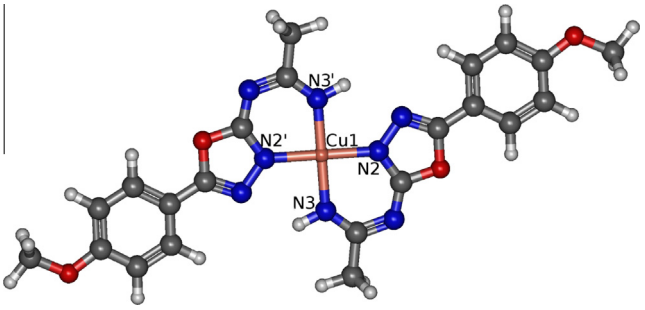

Fig. 1. Structure of the complex bis {N-[5-(methoxyphenyl)-1,3,4-oxadiazole-2-yl] ethanimidamidato}Cu(II) $(C_{11}H_{11}N_4O_2)_2Cu$.

functionals, namely the second generation of type generalized gradient approximation (GGA) called BP86 [21,22], the meta-GGA M06 [23], the global hybrids B3LYP [24,25] and PBE0 [26], and the range-separated hybrids CAM-B3LYP [27] and ωB97x [28] which include an increasing amount of exact Hartree–Fock exchange at long range. Metal atoms were described through relativistic or quasi relativistic core potentials and the associated basis sets [29,30], so that only the valence electrons were treated explicitly, namely the electrons of shells $n = 3$ and 4 for Co, Ni, Cu and Zn, $n = 4$ and 5 for Pd and Cd. The 6-31G+(d) basis sets were used for the other atoms [31].

The initial geometry was taken from the experimental data of L_2–Cu [20]. Harmonic frequency analysis was performed to guarantee that the optimized structures are local minima. Several spin multiplicities were tested for each compound, and the most stable structure was found to be a singlet or a doublet for closed and open shell systems respectively.

Further analysis and characterizations concerning electronic and optical properties were performed at B3LYP and CAM-B3LYP levels. They include calculations of both vertical and adiabatic ionization potentials, the natural population analysis (NPA) [32], and the calculation of the visible–UV absorption spectra in the framework of Time-Dependent DFT (TDDFT) [33–35]. Excited states and charge transfer character of electronic transitions were characterized by plotting the electron density difference between the excited and ground states for the main peaks.

All calculations have been performed using the Gaussian09 suite of programs [31].

3. Results and discussion

3.1. Structure and vibrational analysis of L_2–Cu

Selected bond lengths and angles of the optimized L_2–Cu complex are shown in Table 1. They are calculated with several density functionals and compared to experiment data. All calculated values are in good agreement with the experiments, since all differences between the theoretical and experimental bond lengths are in the 0.01–0.02 Å range. For further analysis, we have selected two density functionals, namely the very popular B3LYP and its long-range corrected version CAM-B3LYP which is expected to better predict the optical properties. Bond lengths and angles implying C and N atoms are given in Table 2. The labeling of atoms can be seen in Fig. 2. CAM-B3LYP is still excellent, but B3LYP is also good. Table 2 gives also the structural parameters of the free ligand, i.e. when it is not in contact to Cu. Two hydrogen atoms was added in the ligand, one H on N2 and one H on N3, to investigate the properties of the free ligand. The complexation with Cu leads to an increasing of the C—N bond lengths, except the N3—C4 bond length which is slightly shortened. The elongation is about 0.1 Å for N1—C2 and C4—N5 bonds.

Major lines in infrared spectra are given in Table 3. The stretching vibrations of N—H, C—C, C—N are clearly identified, as well as two stretching modes implying the copper atom at 697 and 990 cm^{-1} at B3LYP level. The vibrational frequencies are slightly larger at CAM-B3LYP level, and the intensities of the major lines are stronger.

3.2. Structure and electronic properties of L_2–M, M = Co, Ni, Zn, Pd, Cd

We have substituted the copper atom by M = Co, Ni, Zn, Pd and Cd in order to study the influence of the metal and to predict the

Table 2
Selected bond lengths (in Å) and angles (in °) of free L = $(C_{11}H_{11}N_4O_2)$ calculated at B3LYP and CAM-B3LYP levels. Bond and angle values in L_2–Cu complex are also given in parenthesis for comparison to experimental data [20].

	B3LYP	CAM-B3LYP	Expt.
Bonds (Å)			
N1—C2	1.431 (1.317)	1.428 (1.311)	1.311
C2—N3	1.352 (1.350)	1.350 (1.344)	1.346
N3—C4	1.290 (1.321)	1.283 (1.317)	1.329
C4—N5	1.390 (1.334)	1.383 (1.325)	1.325
Angle (°)			
N1—C2—C4	120.7 (125.44)	120.55 (125.46)	125.49
C2—N3—C4	126.0 (119.07)	125.37 (118.85)	118.12
N3—C4—N5	134.5 (133.44)	134.0 (133.31)	133.28
N1—C2—N3—C4	170.8 (180.0)	170.8 (180.0)	177.4
C2—N3—C4—N5	174.6	175.4	177.4

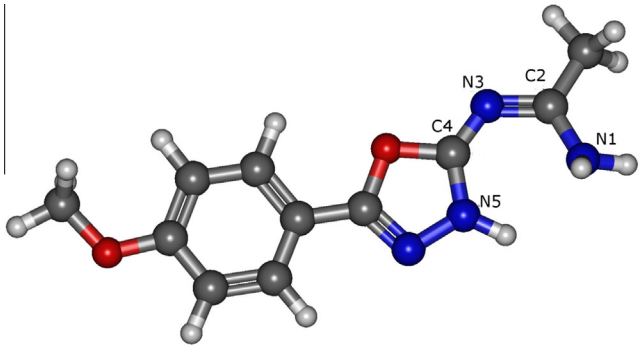

Fig. 2. Structure of the ligand L = $(C_{11}H_{11}N_4O_2)$, N-[5-(methoxyphenyl)-1,3,4-oxadiazole-2-yl]ethanimidamidato.

Table 1
Selected bond lengths (in Å) and angles (in °) of L_2–Cu calculated with several functionals and compared to experiment data [20].

	B3LYP	CAM-B3LYP	BP86	M06	PBE0	wB97X	Exp.
Cu1—N2(Å)	1.959	1.942	1.951	1.939	1.943	1.947	1.940
Cu1—N3(Å)	1.960	1.945	1.955	1.944	1.945	1.952	1.945
N2—Cu1—N3(°)	91.58	91.47	91.05	91.2	91.4	91.65	92.61
N3—Cu1—N2′(°)	88.42	88.53	88.95	88.8	88.6	88.35	87.39
N2—Cu1—N3—N2′(°)	180	180	180	180	180	180	180