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Infrared and electronic spectra of copper (II) complex of maleonitriledithiolate and 4,4′-dimethyl-2, 2′-bipyridine and their theoretical studies

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Abstract

The molecular structure and binding, as well as infrared and electronic spectroscopic properties for the title complex Cu(mnt)(dmbpy) (mnt^{2-} = maleonitriledithiolate, dmbpy = 4,4′-dimethyl-2,2′-bipyridine) were studied in this paper. With semi-empirical PM3 and non-empirical DFT (B3LYP/6-311G*) methods, the molecular geometry of the complex was optimized and corresponding vibrational spectra in the gaseous state were obtained. The calculated results derived from DFT were more reasonable than those from PM3. The point group of Cu(mnt)(dmbpy) in isolated gaseous state was C_2, in which Cu^{II} adopted a distorted tetrahedral geometry and the dihedral angle between the N_2Cu and S_2Cu planes was about 29.814°. And a complete assignment to the IR spectra of such a complicated molecule was exhibited. With ZINDO/S method an electronic spectrum was calculated. The results showed that the calculated values generally agreed with the observed ones. And a detailed explain was made on its electronic spectra.

Keywords: Copper (II) complex; Infrared spectra; Electronic spectra; Quantum calculations

1. Introduction

Over past three decades metal complexes of similar dithiolenes (1,2-dithiolates) [1,2] and diimines [3,4] have been of great interests to inorganic chemists mainly because of their high charge density on delocatized π-electron system. Considerable interests in recent years have been focused on transition–metal complexes with mixed ligands of the type dithiolene and diimine [5–7]. This type of complex have exhibited the intramolecular charge transfer transitions from ligand to other ligand (LL′CT), which are the well-known type of electron transfer transitions in metal coordination compounds and usually exhibit high electrical conductivity, photoconductivity and photochemical properties [8,9].

In previous work, our group has systematically investigated synthesis of the title complexes M(mnt)(dmbpy) (M = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, mnt^{2-} = maleonitriledithiolate, dmbpy = 4,4′-dimetyl-2,2′-bipyridine) [10]. It was found that these complexes have potential applications in the areas of conducting and magnetic materials, as well as non-linear optics. With the mixed nature of the ligands such as pyridyl, methyl and cyanide groups, these complex exhibited a rich vibrational spectra and electron donor–acceptor characteristics. Regarding the importance of these compounds it has been thought useful to study their IR and electronic characterization. Simultaneously theoretical studies on such spectroscopic properties of this type of complexes have not been reported. In this paper emphasis has been placed on geometry

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structure and IR and electronic properties of Cu(mnt)(dmbpy) complex.

2. Experimental

2.1. General materials and physical measurements

For electronic spectrum characterization, *N*,*N*-dimethylformamide (DMF), chloroform, acetone and 1,2-dichloroethane were reagent grade and used without further purification. Na_2mnt, Cu(dmbpy)Cl_2 and Cu(mnt)(dmbpy) were synthesized and characterized according to the published method [10].

Electronic absorption spectra were recorded with a Shimadzu UV-240 Spectrophotometer (190–900 nm). Infrared absorption spectra were obtained at room temperature on a Nicolet-170SX FTIR Spectrometer (4000–400 cm^{-1}, KBr; 500–100 cm^{-1}, CsI).

2.2. Computational details

Applying Polak-Ribiere algorithm of RHF-SCF-PM3 method in the software package of *HyperChem* 7.0 [11] optimized molecular structure and corresponding vibrational spectra were calculated, in which the spin multiplicity of the neuter molecule was chosen as doublet state. The convergence limit was fixed to 1×10^{-8} kcal mol^{-1}, and the criterion of RMS gradient was selected for 2×10^{-5} kcal (mol Ang)$^{-1}$. All the other parameters were performed with the standard parameters as implemented in the software. The results showed that the point group of the molecule was C_{2v} and there were two forms: plane-conformation with two ligands in one plane and vertical-conformation with two ligand-planes were vertical with each other on Cu^{II}.

With the C_{2v} symmetry structure derived from PM3 in the input structure, an UB3LYP (U = unrestricted spin) functions of density functions theory (DFT) [12] on the 6-31G* basis set in the GAUSSIAN 98W program [13], was used to optimize geometry structure and vibrational frequencies. One imaginary vibration (-66.48 cm^{-1} for plane and -58.99 cm^{-1} for vertical) was predicted, which indicating the geometry at which the frequencies were calculated was not a true energy minimum but a transition state. Inspection of the vibrational mode associated with this imaginary vibration showed that two ligands were swing out of plane contrarily about C_2 axis, while Cu^{II} was motionless. It seemed that the ligand dmbpy-plane and mnt-plane could not be in one plane or vertical justly. To discover the true lowest energy structure, a further geometry optimization was carried out, with the use of C_2 symmetry enforcement. No imaginary vibration reflected that the obtained potential surface of the molecule was at the lowest point. The calculated results showed that Cu^{II} adopted a distorted tetrahedral geometry, with a dihedral angle between the N_2Cu and S_2Cu planes.

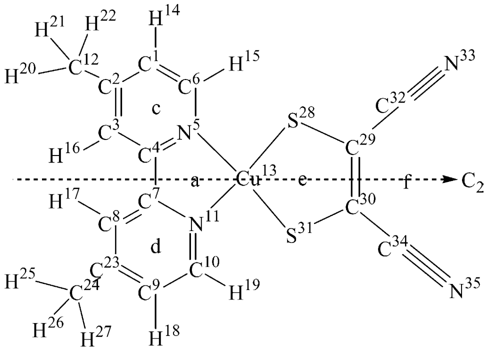

Fig. 1. The structure, orientation axis and labeling scheme (atomic numbering, rings a, c, d, e, fractional plane f) for Cu(mnt)(dmbpy).

With optimized geometry (C_2 symmetry from DFT and C_{2v} symmetry from PM3) of molecular system electronic transition energies and oscillator strengths of the molecule were calculated respectively, employing RHF-SCF-ZINDO/S method in aforementioned *HyperChem* 7.0 software. The configuration interaction (CI) calculations were carried out using singly excited configurations only. The number of singly excited configurations used was 18 occupied and 20 unoccupied orbital.

All computations were gas-phase, i.e., no solvent modeling was included.

3. Results and discussions

3.1. Molecular structure and binding

The chemical structure, labeling atoms, orientation axis and the fractional definitions (ring a, c, d, e and planar f) of the complex were shown in Fig. 1. Selected bond lengths, angles and charges on atom from Mulliken analysis for the equilibrium geometry of the complex predicted with DFT were given in Tables 1–3 respectively, together with the data derived from PM3 method. Because the structure of the complex in the gas phase was unknown and the X-ray diffraction studies for the complex was absent, the geometrical parameters used to illustrate the structure of Cu(mnt)(dmbpy) were

Table 1
Selected bond lengths (*R* (Å)) of Cu(mnt)(dmbpy) in the gaseous state calculated by PM3 and DFT

Bond	*R* (Å)		Bond	*R* (Å)	
	PM3	DFT		PM3	DFT
Cu—N^5	1.886	1.998	Cu—N^{11}	1.886	1.998
Cu—S^{31}	2.136	2.233	Cu—S^{32}	2.135	2.233
S^{31}—C^{30}	1.782	1.756	C^{29}—S^{28}	1.781	1.756
C^{30}—C^{34}	1.412	1.426	C^{29}—C^{32}	1.414	1.426
N^{35}—C^{34}	1.160	1.165	N^{33}—C^{32}	1.161	1.165
N^{11}—C^{7}	1.402	1.354	N^{5}—C^{4}	1.402	1.354
C^{4}—C^{7}	1.417	1.482	C^{29}—C^{30}	1.357	1.376
N^{11}—C^{10}	1.394	1.343	N^{5}—C^{6}	1.393	1.343
C^{23}—C^{24}	1.481	1.506	C^{2}—C^{12}	1.482	1.506