A Polymer \([\text{[Cu}^{II} (\text{Hpb})(\text{mal})] \text{H}_2 \text{O}]_n\): Magnetic Studies and Quantum Chemical Calculation for Its Monomer

ZHU, Hai-Yan

ZHOU, Li-Jun

WANG, Yao-Yu

WEN, Zhen-Yi

WANG, Yu-Bin*

SHANXI KEY LABORATORY OF PHYSICO-INORGANIC CHEMISTRY, DEPARTMENT OF CHEMISTRY, NORTHWEST UNIVERSITY, XI'AN, SHAANXI 710069, CHINA

INSTITUTE OF MODERN PHYSICS, NORTHWEST UNIVERSITY, XI'AN, SHAANXI 710069, CHINA

\([\text{[Cu}^{II} (\text{Hpb})(\text{mal})] \text{H}_2 \text{O}]_n\) (Hpb = 2-2'-pyridylbenzimidazole, mal = maleic acid) is a helical chain-like polymer complex. In order to investigate the electronic structure of the complex, the monomer \(\text{Cu}^{II} (\text{Hpb})(\text{mal})\) was obstructed with different functional groups respectively. For these selective segments, the geometry optimizations were conducted by using hybrid DFT (B3LYP) methods to find that the structure obstructed with \(\text{H}_2 \text{O}\) was better consistent with the experiment, and then this model would be used to latter calculations, such as the frontier molecular orbitals and the NBO charge population analysis. In addition the magnetic behaviors of this complex were analyzed by experiments and the weak antiferromagnetic couple between copper(II) ions was observed. The exchange coupling constant was calculated by DFT based on the spin broken symmetry formalism. The calculated coupling constants were in good agreement with the experimental data.

Keywords polymer, magnetic, quantum chemical calculation, natural bond orbital

Introduction

Over the past decade, studies of polymer complexes have aroused more and more interests of chemists due to their importance to magnetism, transmit-electricity, bioactivity, photic materials and their excellent commercial values, etc. Recently, a new polymer complex \([\text{[Cu}^{II} (\text{Hpb})(\text{mal})] \text{H}_2 \text{O}]_n\) has been synthesized by part of the authors. In order to understand the structural characteristics of the complex, the theoretical calculations might be useful. However it will be a difficult task for such a large periodical system. Considering that the monomer conformational behavior is important to determining many observable properties of a polymer system, a monomer \(\text{Cu}^{II} (\text{Hpb})(\text{mal})\) was intercepted and its boundary atom O in COO could be substituted by OH, OCH_3, or \(\text{H}_2 \text{O}\) to form obstructed system 1, 2 and 3, respectively. Then the structure optimization of the selected monomers can be performed by DFT (B3LYP) with the effective core potential basis set LanL2DZ and the full electron basis set 6-31G(d). It was found that the structure obstructed with \(\text{H}_2 \text{O}\) was better consistent with the experimental results, especially for the B3LYP/6-31G(d) calculation. Thus the latter calculations and discussions, for example, on frontier molecular orbitals and the charge populations on atoms by natural bond orbital would be based on these optimized structures.

As well known, the complexes containing copper(II) often manifest special magnetic properties, and hence we can determine the effective magnetic moment \(\mu_{\text{eff}}\) and the molar magnetic susceptibility \(\chi_{\text{MTH}}\) at different temperatures, from which by fitting the exchange parameter \(J\) can be obtained. We will also calculate the theoretical value of \(J\) by the DFT and the broken symmetry approach.

All calculations were performed with Gaussian 03 program package and run on a PC cluster-deep Comp 1800.

Results and discussions

Structure

The 1D helical chainlike structure of the title complex is shown in Figure 1 and the ORTEP view of the molecular structure and the adopted number scheme is shown in Figure 2. The optimized structures by B3LYP/LanL2DZ and B3LYP/6-31G(d) are displayed in Figures 3 and 4, respectively. Table 1 shows the structural data obtained from X-ray diffraction analysis and the parameters of selected structures from calculations. From Table 1 it can be seen that the B3LYP/LanL2DZ results of structure 2 and structure 3 are similar to the experimental ones, and structure 3 is a little better than structure 2, while the results of structure 1
deviate from the experimental data very much. Moreover, if the optimized structure 3 obtained by B3LYP/LanL2DZ was selected as the initial geometry, the optimization by the all electron basis set 6-31G(d) arrived at more satisfactory accordance with experiments.

**Figure 1** The 1D helical structure of the title complex.

**Figure 2** ORTEP of the title compound with hydrogen atoms omitted for clarity.

**Frontier molecular orbital analysis**

Furthermore, as a representative, some frontier molecular orbital compositions (or atomic orbital populations) of structure 3 by B3LYP/6-31G(d) calculations have been analyzed. The atomic orbital populations for a varied type of atomic orbitals (e.g. s, p, d orbitals) in specific molecular orbitals were expressed as the square sum of atomic orbital coefficients for the type of atomic orbitals. The results are shown in Table 2, and the stereographs of the frontier molecular orbitals and the subfrontier molecular orbitals (NHOMO, HOMO, LUMO and NLUMO) are further displayed in Figure 5 in order to understand their characteristics in detail. From Table 2 and Figure 5, it can be seen that the components of NHOMO and HOMO come mainly from p orbitals of the ligand atoms N(1), N(2) and certain nonligand atoms C of Hpb, a small part from p orbitals of the center metal ion, i.e. they may be characterized by p orbitals. While the components of LUMO come mainly from p and d orbitals of Cu and some nonligand atoms C of mal. For NLUMO, it is mainly composed of p and d orbitals of Cu and certain nonligand atoms C of Hpb, small part from p orbitals of O(2A) and O(3A). It can be summarized that main contributions to the frontier molecular orbitals come from the center metal Cu, ligand atom N 2p and some nonlind atoms C of Hpb. Since properties of a complex is directly correlated with its frontier molecular orbitals, it should be said that some properties of the title compound are mainly determined by center ion Cu and ligand Hpb.

**Natural bond orbital (NBO) analysis**

It is very important to study the regularity of the atomic charge populations of a molecule due to its close relation to charge interactions between the neighboring atoms. According to the natural population and natural electron configuration data showed in Table 3, it can be seen that the natural charge of central Cu(II) is
Table 1  Calculated and experimental bond lengths (nm) and bond angles (°) of different structures

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)—O(1)</td>
<td>0.1830</td>
<td>0.2224</td>
<td>0.2190</td>
<td>0.2224</td>
</tr>
<tr>
<td>Cu(1)—O(2A)</td>
<td>0.1751</td>
<td>0.1950</td>
<td>0.1969</td>
<td>0.1921</td>
</tr>
<tr>
<td>Cu(1)—O(3A)</td>
<td>0.1781</td>
<td>0.2114</td>
<td>0.2108</td>
<td>0.2098</td>
</tr>
<tr>
<td>Cu(1)—N(1)</td>
<td>0.1969</td>
<td>0.2042</td>
<td>0.2045</td>
<td>0.2045</td>
</tr>
<tr>
<td>Cu(1)—N(2)</td>
<td>0.1841</td>
<td>0.1919</td>
<td>0.1945</td>
<td>0.1954</td>
</tr>
<tr>
<td>O(2A)—C(13A)</td>
<td>0.1368</td>
<td>0.1229</td>
<td>0.1249</td>
<td>0.1258</td>
</tr>
<tr>
<td>O(3A)—C(16A)</td>
<td>0.1242</td>
<td>0.1311</td>
<td>0.1317</td>
<td>0.1294</td>
</tr>
<tr>
<td>C(13A)—O(1A)</td>
<td>0.1213</td>
<td>0.1372</td>
<td>0.1277</td>
<td>0.1241</td>
</tr>
<tr>
<td>C(16A)—O(4A)</td>
<td>0.1430</td>
<td>0.1224</td>
<td>0.1260</td>
<td>0.1255</td>
</tr>
</tbody>
</table>

Table 2  Main atomic orbital populations (%) of some frontier molecular orbitals by B3LYP/6-31G(d) calculation

<table>
<thead>
<tr>
<th>Atomic orbital</th>
<th>Cu(1)</th>
<th>O(1)</th>
<th>O(2A)</th>
<th>O(3A)</th>
<th>N(1)</th>
<th>N(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NHOMO</td>
<td>0.39</td>
<td>8.87</td>
<td>2.43</td>
<td>0.12</td>
<td>0.52</td>
<td>0.07</td>
</tr>
<tr>
<td>HOMO</td>
<td>0.41</td>
<td>8.71</td>
<td>2.09</td>
<td>0.36</td>
<td>1.21</td>
<td>0.09</td>
</tr>
<tr>
<td>LUMO</td>
<td>3.79</td>
<td>59.03</td>
<td>19.90</td>
<td>0.41</td>
<td>0.74</td>
<td>0.76</td>
</tr>
<tr>
<td>NLUMO</td>
<td>1.64</td>
<td>50.07</td>
<td>16.52</td>
<td>0.20</td>
<td>2.23</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Figure 5  Stereographs of the NHOMO, HOMO, LUMO and NLUMO (B3LYP/6-31G(d) fully optimized structures).

1.46122e, the charge of the oxygen in H₂O is −0.98655e, while the charges of the oxygen in mal are −0.84748e, −0.67686e, slightly smaller than that in H₂O, and the charges of nitrogen in Hpb are −0.58996e, −0.71497e. The total atomic charge of mal and Hpb are −0.43516e and −0.44234e respectively, which means that 0.43516e was transferred from mal and 0.44234e transferred from Hpb to the central Cu(II) in the process of forming the complex, while the total atomic charges of H₂O (0.01306e) is slightly higher than that of the neutral H₂O molecule, which suggests that the interaction between Cu(II) and H₂O should be weak.

Magnetic properties

Magnetic properties of transition metal complexes have attracted much attention of scientists and a great progress has been made not only in experiments but also in theoretical studies. In this paper the magnetic behavior of the compound was investigated.
Figure 6 plots of molar magnetic susceptibilities $\chi_{MT}$ versus $T$ ($T=79-290$ K) and the effective magnetic moment $\mu_{\text{eff}}$ versus $T$. The $\mu_{\text{eff}}$ value at room temperature was 1.86 $\mu_B$, slightly higher than the spin-only value for Cu(II) ($1.73 \mu_B$). The effective magnetic moment would descend with the decrease of temperature, which suggested an antiferromagnetic exchange interaction within the two Cu(II) ions through the effective exchange media of carboxylate group. For an exchange interaction system the Hamiltonian according to the Heisenberg model can be expressed as:

$$H = -2J \sum (S_i \cdot S_j + \alpha S_i S_j) \quad \alpha < 1$$  \hspace{1cm} (1)$$

where $S_i$ is the spin of the paramagnetic atom at site $i$ and $J$ the exchange coupling constant. The fitting of $\chi_{MT}$ gave $J = -0.5431$ cm$^{-1}$. The formalism for computing the magnetic exchange constant in dinuclear complexes and organic biradicals has been recently reviewed. The exchange coupling constant was determined directly from unrestricted calculations of the triplet. In the next paragraph an expression for the coupling constant was derived:

$$J' = \frac{E_{bs} - E_i}{1 - \langle S^2 \rangle_{bs}/2}$$  \hspace{1cm} (5)$$

or by $E_i = \frac{1}{a^2}(E_{bs} - (1-a^2)E_s)$, a more convenient expression was desired:

$$J' = \frac{2}{\langle S^2 \rangle_{bs}} (E_s - E_{bs})$$  \hspace{1cm} (6)$$

The calculated coupling constant and related quantities are listed Table 4. It can be seen that the calculated values of the coupling constant $J'$ are in excellent agreement with the experimental data. However, it should be pointed out that the excellent agreement between the calculations and experiment is fortuitous since the calculated $J'$ value is a very small quantity obtained from the difference between two large energies, which should be very accurate to guarantee the high accuracy of the small quantity. Though the accuracy requirement might be too high for the present DFT level, the antiferromagnetic coupling is rational because it is believed that the singlet is more stable than the broken singlet or the triplet.

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**Table 3** Natural population and natural electron configuration (B3LYP/6-31G(d) fully optimized structures of some chief atoms

<table>
<thead>
<tr>
<th>Atom</th>
<th>Natural electron configuration</th>
<th>Natural charge/e</th>
<th>Core/e</th>
<th>Valence</th>
<th>Rydberg</th>
<th>Total/e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)</td>
<td>[core] 4s (0.35) 3d (9.15) 4p (0.03)</td>
<td>1.46122</td>
<td>17.99724</td>
<td>9.50101</td>
<td>0.04053</td>
<td>27.53878</td>
</tr>
<tr>
<td>O(1)</td>
<td>[core] 2s (1.76) 2p (5.21) 3p (0.01)</td>
<td>-0.98655</td>
<td>1.99990</td>
<td>6.97073</td>
<td>0.01591</td>
<td>8.98655</td>
</tr>
<tr>
<td>O(2A)</td>
<td>[core] 2s (1.72) 2p (5.12) 3p (0.01)</td>
<td>-0.84748</td>
<td>1.99974</td>
<td>6.83379</td>
<td>0.01395</td>
<td>8.84748</td>
</tr>
<tr>
<td>O(3A)</td>
<td>[core] 2s (1.71) 2p (4.86) 3d (0.02)</td>
<td>-0.67686</td>
<td>1.99972</td>
<td>6.65304</td>
<td>0.02411</td>
<td>8.67686</td>
</tr>
<tr>
<td>N(1)</td>
<td>[core] 2s (1.34) 2p (4.22) 3p (0.02)</td>
<td>-0.58996</td>
<td>1.99930</td>
<td>5.56212</td>
<td>0.02854</td>
<td>7.58996</td>
</tr>
<tr>
<td>N(2)</td>
<td>[core] 2s (1.36) 2p (4.33) 3p (0.02)</td>
<td>-0.71497</td>
<td>1.99924</td>
<td>5.69098</td>
<td>0.02475</td>
<td>7.71497</td>
</tr>
</tbody>
</table>
Coupling constant formalism

As is well known the unrestricted triplet is spin contaminated. Suppose that the contamination comes mainly from the singlet, and then the normalized wave function of the unrestricted triplet can be written as:

$$\psi_{bt} = \frac{1}{\sqrt{1+b^2}}(\psi_s + b\psi_t)$$  \hspace{1cm} (8)

where $\psi_s$ and $\psi_t$ represent the corresponding wave functions of a pure singlet and triplet, respectively. For the unrestricted triplet the expectation value of the operator $\hat{S}^2$ can be expressed as:

$$\langle \hat{S}^2 \rangle_{bt} = \langle \psi_{bt} | \hat{S}^2 | \psi_{bt} \rangle = \frac{1}{1+b^2} \langle \psi_s + b\psi_t | \hat{S}^2 | \psi_s + b\psi_t \rangle$$

$$= \frac{2b^2}{1+b^2}$$  \hspace{1cm} (9)

where the eigenvalue of the operator $\hat{S}^2$ is defined as $2S$ not $2S+1$ in order to keep consistence with Ref. 24 and the output of the Gaussian calculations. The energy of the unrestricted triplet can be written as:

$$E_{bt} = \langle \psi_{bt} | H | \psi_{bt} \rangle = \frac{1}{1+b^2}(E_s + b^2E_t)$$  \hspace{1cm} (10)

Combining Eqs. (9) and (10), the energy of the pure triplet can be obtained:

$$E_t = \frac{(1+b^2)(E_{bt} - E_s)}{b^2}$$  \hspace{1cm} (11)

Thus Eq. (7) can be derived:

$$J = E_t - E_s = \frac{2}{\langle \hat{S}^2 \rangle_{bt}}(E_t - E_{bt})$$

Similar to the familiar broken symmetry formalism, Eq. (7) can be referred to the broken triplet formalism of the exchange coupling constant. The similarity between the both formalism can lead to the formal unity of Eqs. (7) and (6), but it seems that Eq. (7) may be easily used because $E_{bt}$ and $\langle \hat{S}^2 \rangle_{bt}$ can be obtained directly from the output of the unrestricted triplet calculation.

Conclusion

The molecular geometry of the monomer of the title complex calculated by DFT (B3lyp/6-31G(d)) was well agreed with the crystal structure. Analyses of frontier molecular orbital and natural bond orbital indicate that certain properties of the complex were mainly determined by Hpb. Additionally, study on magnetic properties clarified the character of the polymer complex. The molar magnetic susceptibilities exhibited strong temperature dependence in the range of 2—302 K, and the $\mu_{eff}$-$T$ plot showed that the title compound was antiferromagnetic at the normal temperature, and changed to weak ferromagnetic when temperature was decreased to 188 K. The computed $J$ values by two different methods were nicely agreed with the experimental ones.

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References


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