

# Electronic Structure of a Molecular Magnet from Salicylate Based Copper Complex

Nguyen Duc Tho<sup>1</sup>, Nguyen Thuy Trang<sup>1</sup>, Hoang Nam Nhat<sup>1,\*</sup>

<sup>1</sup>VNU University of Engineering and Technology,  
144 Xuan Thuy, Cau Giay, Hanoi, Vietnam

Received 14 September 2012, received in revised form 02 October 2012

**Abstract.** The electronic structure of the metallo-organic compound  $\text{Cu}(\text{SA})_2(2\text{-PM})_2$  (2-PM is 2-pyridylmethanol) is presented. The calculation was performed using the Density Functional Theory with unrestricted spin polarized model and large wave function basis sets which include the polarized and diffuse functions. The single point energy calculation for the isolated molecule gave the HOMO-LUMO separation of 3.8 eV and the LDA+U band structure calculation showed the band gap of only 0.38 eV. The calculated magnetic moment per molecule is comparable to the experimentally observed value.

*Keywords:* Molecular magnet, DFT, Electronic structure

## 1. Introduction

Salicylic acid (SA) in the form of  $\text{C}_6\text{H}_4(\text{OH})\text{COOH}$  is a natural extract from the bark of the willow tree (salix in Latin). It is commonly referred to as a plant hormone due to numerous functions that this compound expresses on the growth and development of plants such as active photosynthesis, chloroplast, ion uptake and endogenic signaling [1]. The derivatives of the SA are widely involved in drugs, e.g. acetylsalicylic acid (aspirin), methyl salicylate (against muscle pain) etc. Since the SA is poorly soluble in water, the pyridine ( $\text{C}_5\text{H}_5\text{N}$ ) is often used as a solvent in chemical synthesis. In the presence of  $\text{Cu}^{2+}$  cations, the metal complex in the form of  $\text{Cu}[\text{SA}]_2[\text{pyridine}]_2$  can be created. These structures have been synthesized for the purpose of introducing the new drug categories with controlled releasing mechanism [2]. Recently, these materials have received renewed interest because they have been found to behave as a molecular magnet with the net magnetic moment of nearly  $1\mu_{\text{B}}$  / molecule [3]. No microscopic study, however, has been made to provide physical insights into the electronic structure of the material. In this work, we report the ab initio study of the electronic structure of  $\text{Cu}[\text{SA}]_2(2\text{-PM})_2$ .

---

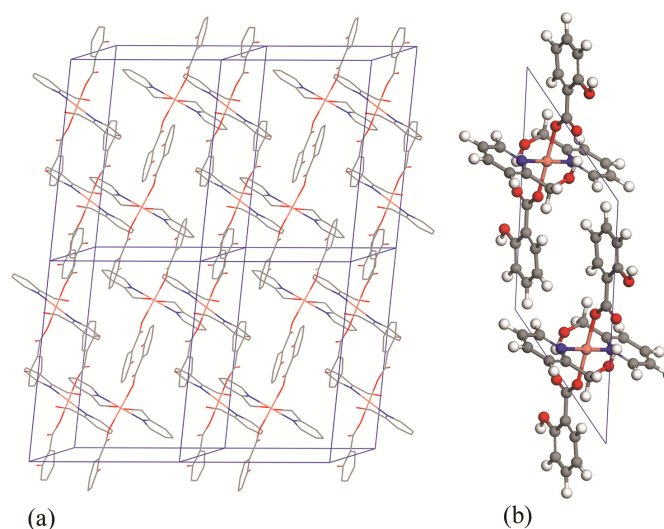
\* Corresponding author.: Email: namnhat@gmail.com

## 2. Experimental

The  $\text{Cu}(\text{SA})_2(2\text{-PM})_2$  (2-PM is 2-pyridylmethanol) has been prepared using the same procedure as reported in Ref. [2], i.e. by mixing of a 0.02M solution of 2-PM with a 0.01M solution of Cu(II) salicylate in continuous stirring in hot methanol. The solution was then left to crystallize from the methanol at room temperature, yielding a prismatic monocrystal of average dimension  $0.25 \times 0.70 \times 0.80$  mm. The relative difference between the measured ( $D_m$ ) and calculated ( $D_c$ ) density  $|D_c - D_m|/D_m$  was less than 0.7%. The compound crystallized in a monoclinic space group  $C2/c$  (no.15) with following lattice parameters  $a = 15.79$ ,  $b = 13.30$  and  $c = 12.08 \text{ \AA}$  ( $\beta = 97.2^\circ$ ). The crystal structure, including unit packing and atomic positions, was determined on the basis of single crystal diffraction technique using  $\text{CuK}\alpha$  radiation (the structural calculation was provided by SHELX-97 software [4]). A total of 3500 diffractions was obtained at room temperature, the maximal  $hkl$  indices were  $(-16, 16)$ ,  $(0, 14)$  and  $(0, 12)$  respectively. The final R-factor was below 4 %. Fig.1 shows the unit packing (a) and the molecular geometry of  $\text{Cu}(\text{SA})_2(2\text{-PM})_2$  (b).

## 3. Method of calculation

The  $\text{Cu}(\text{SA})_2(2\text{-PM})_2$  is quite large system for *ab initio* calculation. A single molecule ( $\text{Cu}_1\text{C}_{26}\text{H}_{24}\text{O}_8$ ) contains 59 atoms and a unit cell 4-times such amount, i.e. 236 in total. For the periodic structure calculation, the minimal set of atomic orbitals should account for 4 Cu, 104 C, 96 H and 32 O atoms. The time consumption of the calculation naturally depends also on the size of  $k$ -vector, size of wave functions, energy or dimension cut-offs, spin model (restricted versus unrestricted spin polarized model) and additional factors. Therefore, to reduce the complexity of the computational task, the appropriate model chemistry should be chosen. However, several factors cannot be simplified, as the  $\text{Cu}(\text{SA})_2(2\text{-PM})_2$  possesses two important electronic properties: (i) it has a doublet ground state due to  $\text{Cu}^{2+} 3d^9$  electronic configuration; (ii) it is expected to be driven by a strong electron-correlation in the Cu-O bonding octahedron. Furthermore, as commonly expected for the metallo-organic compounds containing the benzoyl ring, the molecular orbitals (MO) representing the  $\pi$ - $\pi$  system of the benzoyl ring usually occur as the highest occupied molecular orbital (HOMO), or just immediately below this level. Therefore, the electronic structure of the  $\text{Cu}(\text{SA})_2(2\text{-PM})_2$  was computed in this study with the following settings: (i) the spin model is locked as unrestricted spin-polarized; (ii) the minimal atomic orbital basis set contain polarized and diffuse function; (iii) a reference LDA+U band structure calculation was computed. The used softwares: the Gaussian code [5] was used for the single point (SP) energy calculation for a single molecule; the DMol<sup>3</sup> code [6] was applied for the periodic structure calculation and the CASTEP code [7] was exploited to obtained the LDA+U band-structure.

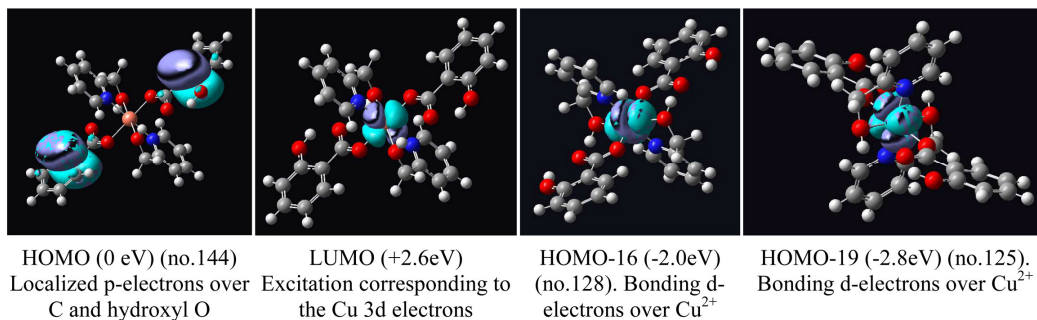


**Fig.1.** The unit cell packing (a) and the molecular structure (b) of  $\text{Cu}(\text{SA})_2(2\text{-PM})_2$ .

#### 4. Results and discussion

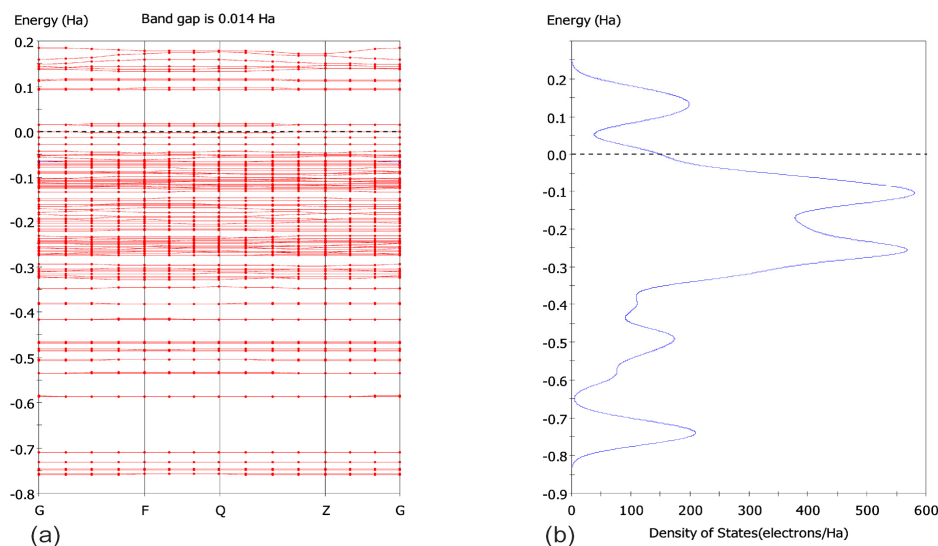
The SP results involved a total of 624 basis functions (1208 primitive Gaussian and 627 cartesian basis functions) for 144 alpha and 143 beta electrons, at the level theory (model chemistry) DFT/UB3LYP/6-31G(d) (Density Functional Theory with Beck's style hybrid functional and unrestricted spin model on a relatively large basis set). The convergence was excellent and we have obtained the correct doublet spin ground state energy,  $E(\text{UB}+\text{HF-LYP}) = -3356.70960979$  Hartrees (Ha), only after 12 cycles of optimization. The HOMO is -0.195 Ha and the lowest unoccupied molecular orbital (LUMO) is -0.056 Ha (Fig.2). As a result, there is a large HOMO-LUMO gap 0.139 Ha (3.8 eV), corresponding to a similar gap in the band-structure (Fig.3). Over  $\text{Cu}^{2+}$ , the Mulliken charge is 0.85 and Mulliken spin density 0.73. The molecule shows no dipole moment but has the quadrupole moment. Only Cu atoms show the non-zeroed spin-dipole coupling. There is a 2.7 Gauss (7.5 MHz) splitting of the hyperfine spin coupling of the  $^{63}\text{Cu}$  EPR resonance expected. The analysis of the Natural Bond Orbitals (NBO) shows the total  $\text{Cu}^{2+} 3d^9$  density is 9.17, of which the density of  $3d_{yz}$  electrons is 1.42, and  $d_{xy}$  1.82, whereas all other 3d-electron densities are near 2.0. A part of the  $\text{Cu}^{2+}$  valence electrons occupies the 4s level (0.34), 4p (0.38, of which  $p_x$  is 0.12,  $p_y$  0.13 and  $p_z$  0.13). The NBO charge over Cu is +1.1 with 18 core electrons and 9.9 valence ones. The NBO electronic configuration for Cu is [core]4s(0.34)3d(9.16)4p(0.38) (of which the 3d alpha and beta contribute 4.95 and 4.21 respectively). The lack of 1 beta electron induced a lower occupation of the  $3d_{yz}$  level (0.42) and the fact that those  $3d_{yz}$  electrons exhibit a highest energy among the 3d electrons. The occupation and energy for the Cu 3d beta (spin down) electrons are listed as follows:  $3d_z^2$  (0.99, -0.292) <  $3d_{x^2-y^2}$  (0.99, -0.284) <  $3d_{xz}$  (0.99, -0.276) <  $3d_{xy}$  (0.83, -0.246) <  $3d_{yz}$  (0.42, -0.161). There is about 2.2eV

separation between the  $3d_{yz}$  and the remaining beta electrons. The lower distribution of charge over the Cu site than the nominal value  $2+$  agrees with the positive densities of the Cu  $4s$  and  $4p$  electrons. However, this does not automatically imply that the oxidation state of Cu is rather  $1+$  than  $2+$ , since the calculated densities may be the false results of the dynamic charge relocation between the Cu  $3d$ - $4s$  levels as experimentally observed in some copper oxide compounds (e.g.  $\text{CuO}_2$  in Ref. [8]). The difference between the spin densities of alpha and beta electrons (0.58) is somewhat lower than the experimentally detected magnetic moment  $\mu_B$  per molecule (0.74) [3].



**Fig.2.** (Color online). The HOMO, LUMO and some other MO-s for  $\text{Cu}(\text{SA})_2(2\text{-PM})_2$ .

The spectral computation of IR spectroscopy showed that the free molecule  $\text{Cu}(\text{SA})_2(2\text{-PM})_2$  exhibits a characteristic IR-active vibration of the carboxyl carbon ( $\text{C}=\text{O}$  resonance) in the static host lattice of the rest atoms at  $1810\text{ cm}^{-1}$ . Another typical vibration is from the hydrogen of the methyl hydroxyl group at  $4095\text{ cm}^{-1}$  ( $\text{O-H}$  resonance). The nuclear magnetic resonance (NMR)  $^{13}\text{C}$  chemical shift for the carboxyl carbon showed the largest value of 149.4 ppm with respect to TMS among the rest carbon atoms. The relatively large  $^1\text{H}$  chemical shift also demonstrated the methyl hydroxyl hydrogen (5.0 ppm).



**Fig.3.** (Color online). Band structure (a) and density of state (b) of  $\text{Cu}(\text{SA})_2(2\text{-PM})_2$ .

The periodic structure calculation was performed with GGA/BLYP functional with a double-numeric wave function basis set DNP 3.5 (which contains polarized and diffuse function). The orbital cut-off was set at  $4.4\text{\AA}$ . The core treatment followed the Effective Core Potentials (ECP) method and the SCF (self-consistent-field) tolerance was set at  $10^{-5}$ . A medium size  $k$  vector was used. Fig. 3(b) shows the band structure, which is comparable to the one obtained by the DNP basis set using DMol<sup>3</sup> code. From this figure the band gap of 0.38 eV was deduced. Fig.3(a) shows the obtained density of state (DOS). The band structure was computed using the LDA+U correction for the Cu 3d electron Coulomb repulsion ( $U=3.5\text{eV}$ ).

## 5. Conclusion

The ferromagnetic ground state was observed for the  $\text{Cu}(\text{SA})_2(2\text{-PM})_2$  with molecular magnetic moment of order  $0.58\mu_B$ . This lower value compared to the observed one may be associated with the dynamic hopping of Cu 3d electrons. The band-structure showed the small band-gap of 0.38 eV which is in sharp contrast to 3.8 eV HOMO-LUMO separation. This signified the important role of the intermolecular hydrogen bonding system which forms the unit cell packing in modifying the semiconductor band-gap.

**Acknowledgments.** The authors would like to thank the QGTD 09.04 project from VNU HN and National Foundation for Science and Technology Development, Vietnam (NAFOSTED) for financial supports (Project Nanofluids and application, 2009, code 103.02.19.09).

## References

- [1] S. Hayat, A. Ahmad (2007). Salicylic acid - A Plant Hormone. Springer. ISBN 1402051832.
- [2] N.N. Hoang, F. Valach, M. Dunaj-Jurco and M. Melnik. Acta Cryst. C48 (1992) 443.
- [3] N.N. Hoang. Unpublished data (2010).
- [4] G. M. Sheldrick. Acta Cryst. A64 (2008), 112.
- [5] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., Gaussian 03, Revision B.03, Gaussian, Inc., Pittsburgh PA, 2003.
- [6] B. Delley, J. Chem. Phys. 92, 508 (1990); Int. J. Quant. Chem. 69, 423 (1998); J. Chem. Phys. 113, 7756 (2000); A. Kessi and B. Delley, Int. J. Quant. Chem. 68, 135 (1998) (DMol<sup>3</sup> code).
- [7] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson, M. C. Payne, Zeitschrift für Kristallographie 220 (5-6) 567 (2005). (Castep code).
- [8] J. M. Zuo, M. Kim, M. O'Keeffe and J.C.H. Spence, Nature 401, 49 (1999).