



# Electronic structure and spectra of cupric acetate mono-hydrate revisited

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## ABSTRACT

The electronic structure and spectra of cupric acetate mono-hydrate were investigated by measuring magnetic susceptibility from 2–300 K, temperature dependence of electronic spectra in EPA solutions and DFT calculations. A comparison of electronic spectra at 300 K and 77 K revealed four isosbestic points indicating the coexistence of the triplet and singlet bands. Calculations showed that the Cu  $3dx^2 - y^2$  orbitals are strongly bonded with the acetate groups and that there was no obvious direct overlap of Cu–Cu  $\delta$ -type orbitals in the singlet ground state. The magnetic interaction energy  $J$  was estimated using the unrestricted MO calculation and HOMO–LUMO mixing method. The UKS HOMO indicated the importance of the super-exchange interaction via the acetate group. Assignments of electronic spectra are presented for the singlet and triplet bands by the TD-DFT method. Polarization characteristics are explained for the visible and near-UV electron transfer band between the two Cu ions proposed by Yamada et al. [S. Yamada, H. Nakamura, R. Tsuchida, Bull. Chem. Soc. Jpn. 30 (1957) 303].

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## 1. Introduction

In the last several decades, a very large number of papers have been published on the magnetic [1–7], structural [8] and the spectral [9–14] properties of di-nuclear cupric acetate mono-hydrate (Scheme 1).

Despite many theoretical papers that have been published up till now [15–18], a reasonable interpretation of the bonding, magnetic and electronic excited states has still to be made. Recently the DFT and TD-DFT methods have been applied to  $d^6$  metal complexes [19]. In this paper we present new experimental results on the electronic spectra of cupric acetate mono-hydrate in EPA solutions together with results of uB3LYP calculations on the singlet and the triplet states. Electronic absorption bands were assigned by the TD-DFT method and a new interpretation of the visible and UV bands is presented which involves the configuration interaction of orbitals of Cu and carboxylate groups. We confirmed the presence of the electron transfer band polarized along the Cu–Cu bond [9] by showing that it was a HOMO to LUMO transition. Assignment of the electronic spectra covering the singlet and the triplet states is presented for the first time. The magnetic interaction energy  $J$  is calculated showing the super-exchange interaction through the carboxylate groups between the Cu–Cu bond.

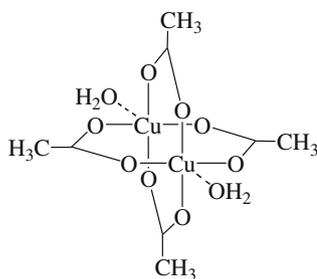
## 2. Results and discussions

### 2.1. Magnetic susceptibility

The magnetic susceptibility of cupric acetate dihydrate was measured by a SQUID (Quantum Design, MPMS-5s) magnetometer for 2–300 K and that at 300 K was determined by the Gouy method. The temperature dependence of susceptibility was analyzed by assuming the singlet and the triplet states, and the magnetic interaction energy  $J$  was estimated as  $-298 \text{ cm}^{-1}$  which was in agreement with the previous studies.[3,7] The occupancy of the triplet state was estimated as 41.8% at 300 K and 1.2% at 77 K using this value of  $J$ .

The value of  $J$  was calculated by the DFT method using several basis sets. In the calculation process, the restricted Kohn–Sham (RKS) type MO is calculated first, and then the unrestricted Kohn–Sham (UKS) type MOs of the singlet and the triplet states are obtained by HOMO–LUMO mixing of the RKS MO. The structure of cupric acetate mono-hydrate was optimized by minimizing the total energy of the UKS calculation. The optimized Cu–Cu distance was compared with the X-ray result [8] as shown in Table 1 and the energy difference between the singlet and the triplet states was compared with experimental  $J$  values. These results were dependent on the basis sets, as shown in Table 1. Though LanL2DZ gave the best result for  $J$ , but as 6-31G(d) is better than other basis sets for spectral studies by the TD-DFT method, the following discussions is based on calculations using the 6-31G(d). All calculations are performed by *g03* program [20] and some of calculations were done at Computational Science Center, Okazaki, Japan.

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Scheme 1.

Table 1

Experimental Cu–Cu distance and  $J$  value. The calculated results by different basis sets are shown for comparison.

	Exp. value	LanL2DZ	6-31G	6-31G(d)
Cu–Cu (Å)	2.633 [8]	2.726	2.666	2.549
$J$ (cm <sup>-1</sup> )	-298	-295	-35	-201

## 2.2. Cu–Cu bonding in Cu-acetate

The  $\alpha$ - and  $\beta$ -spin HOMOs of the singlet state are shown at the bottom of Fig. 1. A remarkable feature is the localization of Cu  $3dx^2 - y^2$  orbital on the left and the right sides as described by the valence bond theory which is useful for strongly spin-correlated systems. Moreover, the  $\alpha$ - and  $\beta$ -HOMOs extend to acetate groups with different shapes, resembling those of the triplet state of Na-acetate. This means that the spin correlation extends to the acetate groups. The direct overlap between the Cu  $3dx^2 - y^2$  orbital is not obvious as is required by the  $\delta$  bond theory [3,21]. If there is bonding interaction between Cu  $3dx^2 - y^2$  orbital, there would be accumulation of charge density between them in DFT MOs. Our results show the coupling of spin in the Cu  $3dx^2 - y^2$  orbital occurs through super-exchange via acetate groups. The super-exchange theory for metal-oxides was proposed by Kramers [22] and Anderson [23]. The importance of the super-exchange interaction via acetate groups has been discussed in earlier experimental studies [2,7].

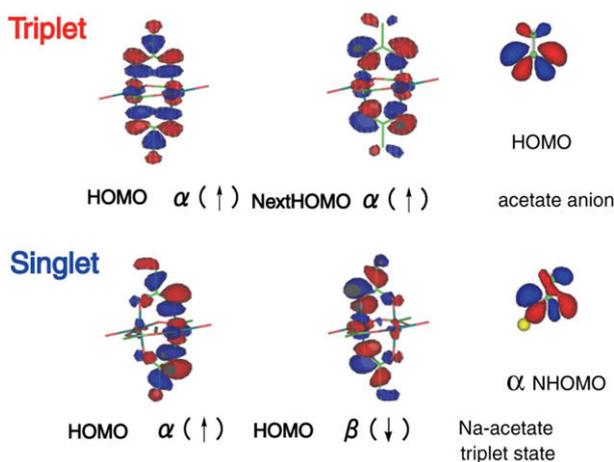


Fig. 1. Unrestricted type Kohn-Sham (UKS) HOMO and next HOMO for the triplet state and  $\alpha$ - and  $\beta$ -spin HOMOs of the singlet state of Cu-acetate. The parts of MOs on the two of four acetate groups are omitted for clarity of illustration. In the right upper side, the HOMO of acetate anion is shown which is involved in the next HOMO of the triplet state of Cu-acetate. In the right bottom side, the  $\alpha$ -NHOMO of Na-acetate is shown which is involved in the  $\beta$ -HOMO of the singlet state of Cu-acetate.

In the  $\alpha$ -HOMO of triplet state, the two Cu  $3dx^2 - y^2$  orbitals form symmetrical combination while they form anti-symmetrical combination in the  $\alpha$ -Next HOMO (NHOMO). The mode of coupling of two Cu  $3dx^2 - y^2$  orbitals is bonding and anti-bonding of the  $\delta$  bond, however, the sequence of energy level is reversed that the  $\delta$  bond between the Cu  $3dx^2 - y^2$  orbitals is not supported from the DFT calculation. The  $\delta$  bond is unlikely since the overlap of the wave function is not found between Cu  $3dx^2 - y^2$  orbitals.

The coupled orbitals of acetate groups are shown in the right column of Fig. 1 for the triplet and single states. In the  $\alpha$ -Next HOMO (NHOMO) of triplet state, the HOMO of acetate anion is coupled with the anti-symmetrical combination of two Cu  $3dx^2 - y^2$ . In the  $\alpha$ -HOMO of triplet state the NHOMO of acetate group is coupled in out of phase with symmetrical combination of two Cu  $3dx^2 - y^2$ . This result shows more importance of coupling of Cu  $3dx^2 - y^2$  with acetate groups in determining energy level in bonding of two Cu ions. In the singlet state of Cu-acetate, the orbitals of acetate groups are those of the triplet state, which means that the spin polarization extends to the acetate groups to form the bonding of two Cu ions. These results support the super-exchange theory of Cu–Cu bonding.

## 2.3. Electronic spectra

Electronic spectra were measured at 77 K and 300 K in mixed solvent of ethylether 5, isopentane 5 and ethanol 2 (EPA) solutions as shown in Fig. 2. In non aqueous solvents, cupric acetate monohydrate exists in dimeric form as evidenced by magnetic measurements [5]. The electronic spectra at 300 K include both the triplet and the singlet bands, while the spectra at 77 K show only the singlet bands. Dubicki [11] demonstrated the contribution of the triplet state by showing that there were temperature independent isosbestic points in crystalline spectra at 340 nm and 420 nm. We also found these points as well as other isosbestic points at 710 nm and 520 nm. Graddon [12] measured spectra in chloroform solutions and Reimann et al. [13] measured crystalline spectra and showed additional lowest energy band at 900 nm region. In the present spectra the peaks of singlet bands are indicated as (1), (2) and (3) in Fig. 2 and the shoulders marked as (4) and (5) are assigned to triplet bands.

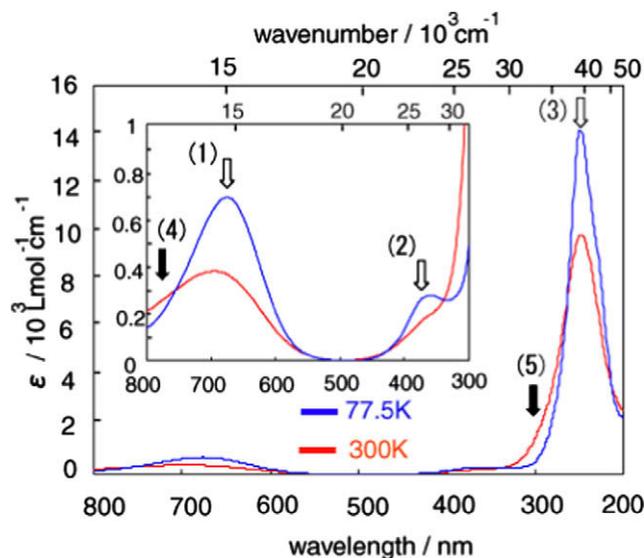


Fig. 2. Temperature dependence of electronic absorption spectra of cupric acetate in EPA solution. Arrows indicate position of singlet (1), (2) and (3) and triplet bands (4) and (5), respectively.

**Table 2**

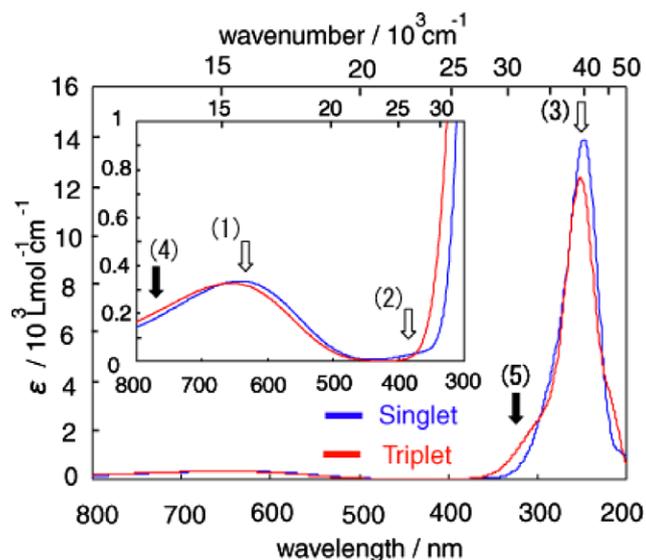
Experimental and calculated energies and intensities of electronic absorption bands. The results are sensitive to the structure that three models obtained by (A) LANL2DZ; (B) 6-31G and (C) 6-31G(d) are used for the calculation of excited states by 6-31G(d).

	Exp. values (nm, f-value)	A (nm, f-value)	B (nm, f-value)	C (nm, f-value)
Band (1)	676 (0.0060)	694 (0.0080)	705 (0.0030)	637 (0.0041)
Band (2)	360 (0.0044)	309 (0.0011)	364 (0.0006)	363 (0.0008)
Band (3)	248 (0.300)	299 (0.3038)	251 (0.293)	246 (0.267)
Band (4)	800 (0.004)	810 (0.006)	800 (0.003)	890 (0.003)
Band (5)	310 (0.035)	330 (0.045)	330 (0.01)	300 (0.04)
Band (6)	260 (0.20)	260 (0.22)	280 (0.22)	280 (0.19)

We performed TD-DFT calculations on the singlet and the triplet bands with 6-31G(d) basis on the structures optimized by three basis sets as shown in Table 2. The agreement of the calculated energies with experimental peak positions is quite satisfactory by the structure obtained by 6-31G(d), but intensities were better using a structure optimized by LANL2DZ basis. Thus the calculated results are strongly dependent on the model structure of cupric acetate mono-hydrate. In Table 2, band (1) is shown as a single band but it includes several weak excited states of comparable intensities. Experimentally it has been found that there are several bands in this region [12,13]. In Fig. 3 the simulated spectra calculated with 6-31G(d) basis for a structure optimized by the same basis have been visualized using GAUSSVIEW program.

#### 2.4. $\sigma$ - $\sigma^*$ Transitions of Cu-O bonds

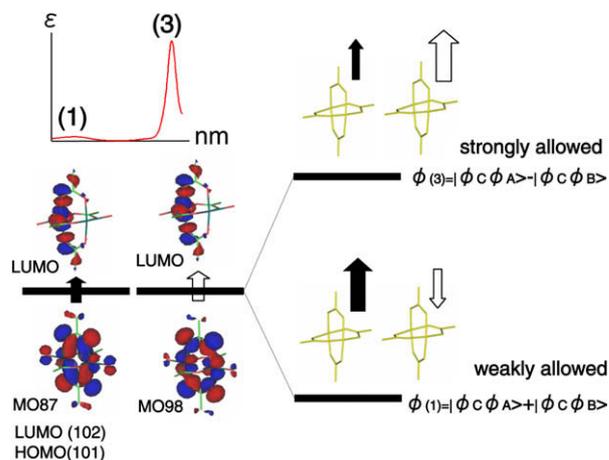
In earlier theoretical analysis of the visible absorption spectra of cupric acetate [12,16–18,21], the d-d transitions of Cu<sup>2+</sup> ions were considered to be the origin of the visible band and near-UV band. However, the observed absorption intensity is much greater than that expected from the d-d transition, and therefore an alternative interpretation is needed for correct assignment of the visible band.



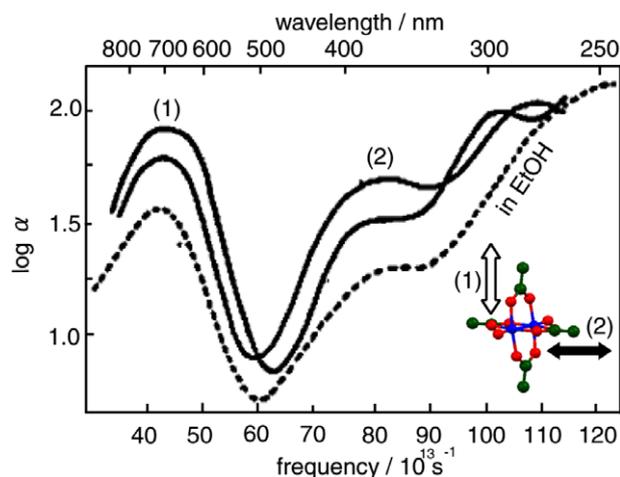
**Fig. 3.** Simulation of singlet (1), (2) and (3) and triplet (4) and (5) bands by the TD-DFT method using 6-31G(d) basis on the optimized structure obtained by 6-31G(d) by GAUSSVIEW. The triplet band (6) is not shown since it is overlapped with (3).

TD-DFT calculations showed that the weak visible band (1) and strong UV band (3) appeared as the result of a configuration interaction between the  $\sigma$ - $\sigma^*$  transitions of the Cu-O bonds. Typical MOs involved in such excitation are shown in Fig. 4, where  $|\phi_C\phi_A\rangle$  means that an electron in  $\phi_A$  is excited to  $\phi_C$  and  $\phi_A$  is MO87 and  $\phi_C$  is LUMO as shown in Fig. 4 and  $\phi_B$  is MO98. Since  $\phi_C$  is symmetric to the  $xz$  plane and  $\phi_A$  and  $\phi_B$  have a node on the  $xz$  plane; then transitions from  $\phi_A$  and  $\phi_B$  to  $\phi_C$  are allowed for light polarized along the  $y$ -axis. This is consistent with the crystalline spectra [9] which showed that the visible band is polarized perpendicular to the Cu-Cu bond axis as shown in Fig. 5.

The MOs of Fig. 4 are not spin specified, since the  $\alpha$ -spin and the  $\beta$ -spin MOs are equally involved, and only the largest contributing MOs are illustrated for brevity. On the right side of Fig. 4, the modes of configuration interaction for the weak visible and strong UV bands are illustrated, in which the coupling of transition moments produces weak and strong bands. The polarization of these transitions are perpendicular to the Cu-Cu axis or parallel to the  $y$ -axis. The calculated results indicated many excited configurations, but we show only the most important ones in Fig. 4.



**Fig. 4.** Configuration interaction of two type electronic excitations  $|\phi_C\phi_A\rangle$  and  $|\phi_C\phi_B\rangle$ , which gives weak visible band (1) and strong UV band (3). The arrows show components of transition moments. Only the  $\alpha$ -spin LUMO is shown although the  $\beta$ -spin one is equally involved.



**Fig. 5.** Single crystalline absorption spectra of cupric acetate mono-hydrate as reported by Yamada et al. [9]. The inserted crystal structure is from Ref. [8].

### 2.5. Electron transfer band (2) of Tsuchida and Yamada

In 1957 Yamada et al. [9] presented the single crystalline absorption spectra of cupric acetate mono-hydrate shown in Fig. 5. For polarization, it is most important that the visible and the UV bands are perpendicular to the Cu–Cu axis, while the near-UV band at 370 nm is along the Cu–Cu direction [12]. Tsuchida and Yamada proposed that the 370 nm band is due to electron transfer between the two  $\text{Cu}^{2+}$  ions, though, no theoretical interpretation of this has yet been proposed. The TD-DFT calculation shows that this band is the excitation from the  $\alpha$ -HOMO to the  $\alpha$ -LUMO and from the  $\beta$ -HOMO to the  $\beta$ -LUMOs as shown in Fig. 6. Since the HOMO is anti-symmetric to the  $xy$ -plane and the LUMO is symmetric, the transition is allowed for light polarized along the Cu–Cu axis ( $z$ -axis). Moreover, as the Cu  $3d_{x^2-y^2}$  orbital and the associated  $\sigma$ -orbitals of O of the acetate are localized on one side, there is electron transfer from the right side orbitals in the  $\alpha$ -HOMO to the left side orbitals of  $\alpha$ -LUMO and the transfer is in the opposite way to the  $\beta$ -LUMO from  $\beta$ -HOMO. This is consistent with intuitive interpretation of Tsuchida and Yamada on their experimental results [9].

### 2.6. Electronic transitions of triplet states

There are two extra absorption bands, (4) and (5), in the spectra at 300 K as compared to those at 77 K as shown in Fig. 2 and accordingly, these two bands are attributable to those of the triplet state. TD-DFT calculation for the triplet excited states indicated three bands (4), (5) and (6) (Table 2), of which band (6) is not resolved since it overlaps with band (3). Both bands (4) and (5) include several excited configurations, and their composite MOs are shown in Fig. 7. Since the  $\beta$ -MOs 101 and 102 are vacant and the  $\alpha$ -spin MOs are filled up to MO102, excited configurations of triplet bands (4) and (5) appear due to excitation from  $\beta$ -MOs 99, 100, 101 and 102 as shown in Fig. 7. Two absorption bands in the visible and the near-UV region appear by configuration interaction of these four MOs.

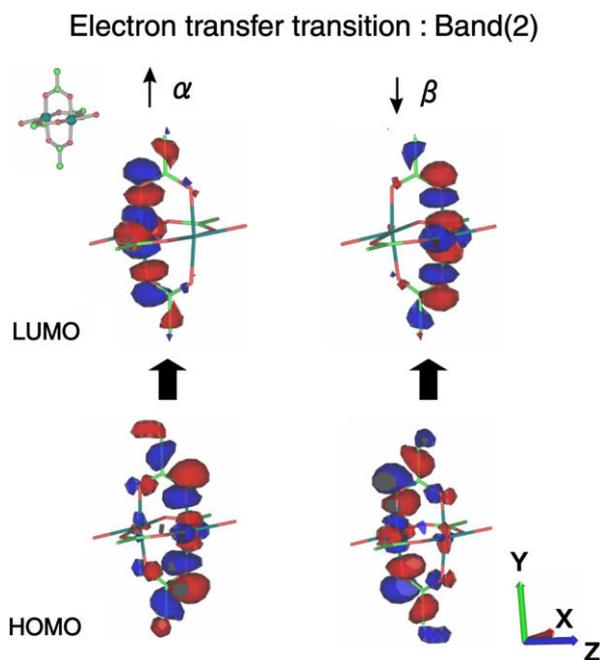


Fig. 6. The MOs concerning the electronic transition of band (2).

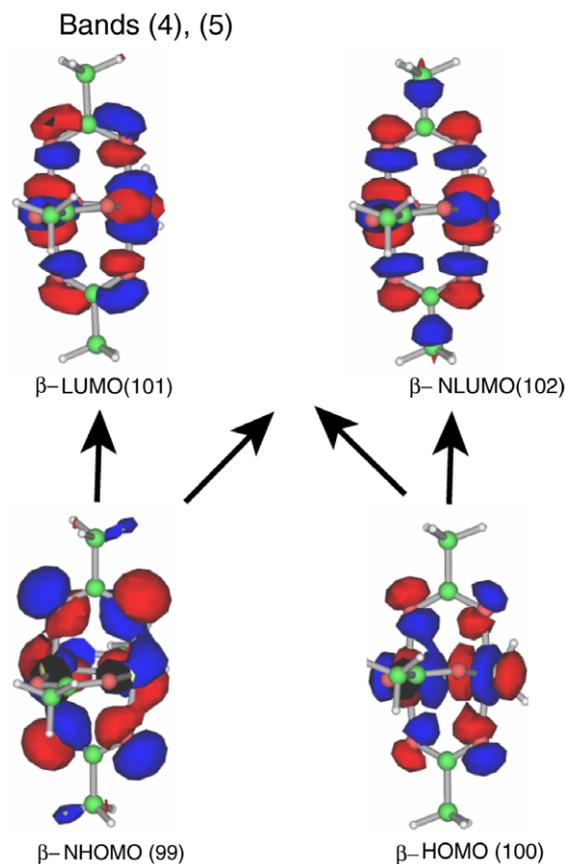


Fig. 7. Important MOs concerned with the excitation of triplet state.

In conclusion we showed performance of DFT calculation for the analysis of the nature of chemical bonding of Cu–Cu di-nuclear acetate and magnetic properties. TD-DFT method is shown to be useful for accurate analysis of the electronic spectra to clarify the nature of the excited states.

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