Thermochromism and Magnetic Susceptibility of Copper(II) Anthracene-9-carboxylate

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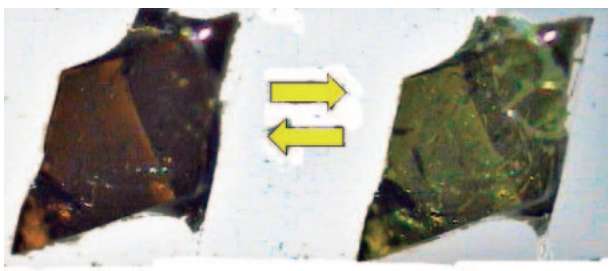
We investigated the thermochromism of copper(II) anthracene-9-carboxylate experimentally and theoretically. We performed X-ray crystal structure analysis at 233 and 113 K, measured magnetic susceptibility for 300–2 K, diffuse reflection spectra at 300 and 77 K, and spectra of the molecule in EPA solution at 300 and 77 K. DFT and TD-DFT calculations were performed to discuss magnetic properties and electronic spectra. The thermochromism was ascribed to a decrease in occupancy in the triplet state at 300 K due to a drop in temperature, since the LMCT band of the triplet state (^{3}LMCT) at 510 nm diminished with a decrease in the population of triplet state at lower temperature. The assignment of electronic absorption bands and the nature of chemical bonding are discussed with the results of DFT and TD-DFT calculation.

We have known about the chromotropism of organic and inorganic crystals for a long time[1–3] and recent progress in investigating that for inorganic complexes has been documented in a comprehensive book.[4] For organic crystals, recent precise X-ray crystal structure analysis has revealed that prototropic transformation[5] and π–π to σ-bonding changes[6] lead to thermochromism. For copper(II) complexes, thermochromism occurs in bis(*N*,*N*-diethylethylenediamine)copper(II) perchlorate accompanied by crystalline structural changes,[7] but the details of spectral changes have not been fully clarified. For bis(1,3-diazacyclooctane)copper(II) complex, thermochromism was observed at 90 °C but the reason for the color change has not been determined yet.[8] Thermochromism has been observed for some iron complexes[9,10] accompanied by changes in magnetic susceptibility, but a structural analysis has not been performed, and the reason for the color change is not understood with respect to magnetic properties.

In a continuation of our study on the magnetic and optical properties of copper(II) carboxylates,[11] we found that the crystal of copper(II) anthracene-9-carboxylate exhibits a conspicuous thermochromism as shown in Figure 1. X-ray crystal structure analysis performed at 233 and 113 K reveals few changes in the structure of molecules and crystalline packing. So the change in color cannot be due to a structural change of molecule in the crystal and must have another explanation. In this study we measured the magnetic susceptibility of the crystal between 300 and 2 K and showed that both the triplet and singlet species were present above 120 K. The change in color of the crystal was confirmed by measuring temperature dependence of diffuse reflection spectra, and the visible and UV spectra at room temperature and 77 K in EPA (ether, pentane, and alcohol mixed solvent) solution. The nature of the excited state was investigated by means of TD-DFT calculations using Gaussian03 program.[12] We established that the thermochromism was due to a decrease in population of the triplet state in dropping from room temperature to a lower temperature.



223 K 80 K

Figure 1. Reversible color change of the crystal. At 223 K (left) the color of the crystal is brown and it changes to light green at 80 K (right).

Experimental

Materials. Copper(II) anthracene-9-carboxylate was synthesized as follows. To an ethyl acetate solution (20 mL) of anthracene-9-carboxylic acid (22.3 mg) a methanol solution (30 mL) of copper(II) acetate monohydrate (10.2 mg) was added. After the mixture stood for several days at room temperature, dark brown plate-like crystals were precipitated. $[Cu_2(O_2CC_{14}H_9)_4(CH_3OH)_2]\cdot CH_3OH$ Anal. Calcd for $C_{63}H_{46}Cu_2O_{11}$: C, 68.41; H, 4.19%. Found: C, 68.47; H, 4.18%.

Thermochromism of Crystal. When a crystal was cooled from 223 to 80 K, the color of a single crystal changed as shown in Figure 1. As the color change was reversible, it was due to thermochromism.

Crystal Structure. Single-crystal X-ray diffraction data were collected with a Rigaku MERCURY CCD system diffractometer using Mo Kα radiation ($\lambda = 0.7107$ Å).

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Table 1. Selected Bond Lengths/Å and Angles/° for at 233 and 113 K

	233 K	113 K	DFT calculation
Interatomic distances			
Cu_1–Cu_2	2.6042(18)	2.5967(10)	2.635
Cu–O(carboxylate)(av)[a)]	1.965(1)	1.965(8)	1.996
Cu–O(methanol)(av)[a)]	2.150(1)	2.140(4)	2.197 (H_2O)
Dihedral angles			
C(1)–O(1)–O(2) plane and Plane A	46.32(8)	46.69(1)	55.8
C(46)–O(7)–O(8) plane and Plane B	103.39(5)	101.67(3)	123.2
C(16)–O(3)–O(4) plane and Plane C	105.15(8)	104.92(1)	123.2
C(31)–O(6)–O(5) plane and Plane D	60.12(0)	60.09(5)	55.8
Plane A and Plane C	85.64(4)	85.62(7)	94.15
Plane B and Plane D	70.03(1)	68.75(8)	90.95

a) Average of eight independent values.

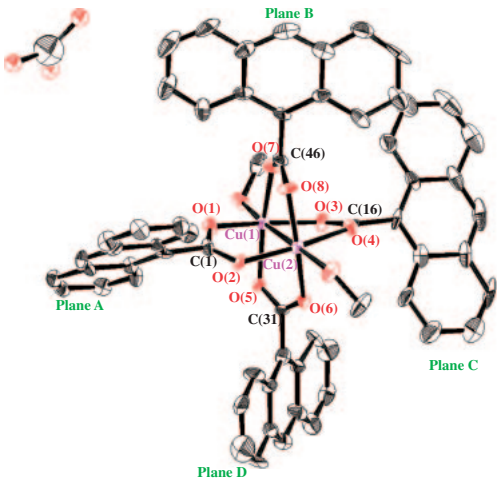

Figure 2. ORTEP drawing of $[Cu_2(O_2CC_{14}H_9)_4(CH_3OH)_2]\cdot CH_3OH$ at 233 K (phase **1**) with the asymmetric unit shown with displacement ellipsoids at the 35% probability level. Hydrogen atoms are omitted for clarity.

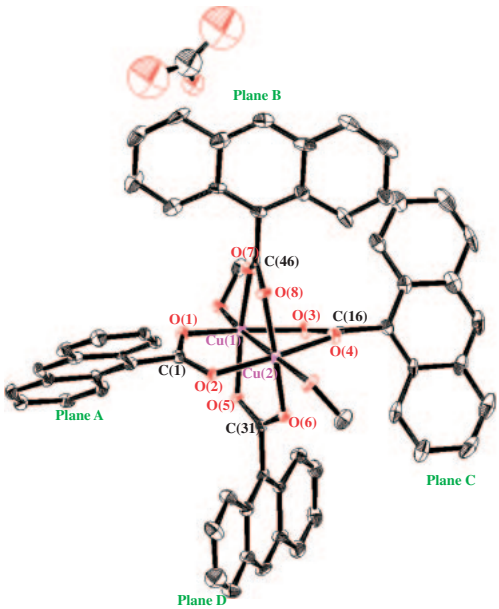

Figure 3. ORTEP drawing of $[Cu_2(O_2CC_{14}H_9)_4(CH_3OH)_2]\cdot CH_3OH$ at 113 K with the asymmetric unit shown with displacement ellipsoids at 35% probability level. Hydrogen atoms are omitted for clarity.

The crystallographic data at 233 K were as follows: monoclinic, $C2/c$ (No. 15), $a = 26.50(7)$, $b = 14.25(6)$, $c = 28.32(8)$ Å, $\beta = 103.97(2)°$, $Z = 8$, $\mu = 8.85\,cm^{-1}$, 43231 reflections measured, 11580 unique, $R_1 = 0.066$, $R_w = 0.161$ ($I > 2.00\sigma(I)$). They have been deposited in Cambridge Crystallographic Data Centre: Deposition number CCDC-606839.

The crystallographic data at 113 K were monoclinic, $C2/c$ (No. 15), $a = 26.338(16)$, $b = 14.22(3)$, $c = 28.27(3)$ Å, $\beta = 104.447(15)°$, $Z = 8$, $\mu = 8.95\,cm^{-1}$, 43820 reflections measured, 11518 unique, $R_1 = 0.059$, $R_w = 0.090$ ($I > 2.00\sigma(I)$). These data have also been deposited in Cambridge Crystallographic Data Centre: Deposition number CCDC-606840.

Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; e-mail: data_request@ccdc.cam.ac.uk).

Views of the molecules at 233 and 113 K are shown in Figures 2 and 3, respectively. Four anthracene-9-carboxylate groups and two methanol molecules surround the two Cu^{2+} atoms. The Cu–Cu distances are 2.6042(18) and 2.5967(10) Å at 233 and 113 K, respectively. Copper(II) ions are joined by eight oxygen atoms of four anthracene-9-carboxylates, which is a common structural feature of copper(II) carboxylates. Two of three methanol molecules are coordinated with each Cu atom, while one is in a disordered state with occupancy factors for O_{11}, O_{12}, and O_{13} of 0.30, 0.30, and 0.40, respectively. Selected bond lengths and dihedral angles at 233 and 113 K are given in Table 1. As the difference in structure between 233 and 113 K was only a slight, the change in color is not due to a conformational change of molecule in the crystal.

Results and Discussion

Diffuse Reflection Spectra. Diffuse reflection spectra were measured using a JASCO V 560 spectrophotometer at 300 and 77 K as shown in Figure 4. In the spectrum at 300 K, an extra reflection peak was observed at 510 nm and its color was brown.

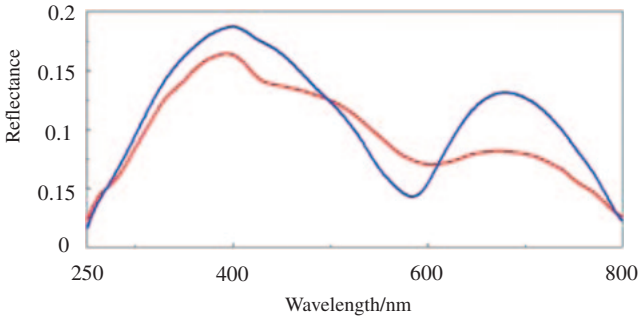

Figure 4. Diffuse reflection spectra of copper(II) anthracene-9-carboxylate measured at 300 (red line) and 77 K (blue line).

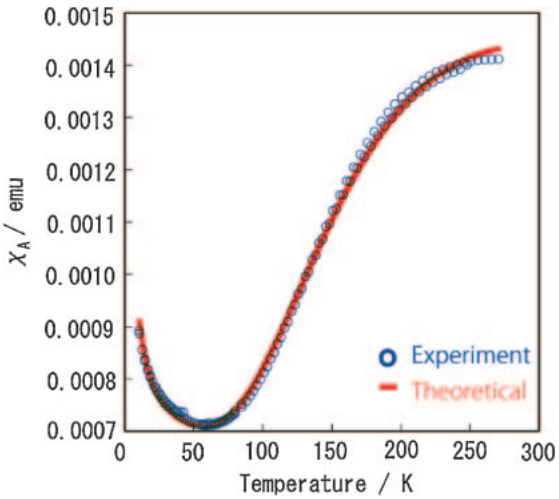

Figure 5. Magnetic susceptibility of copper(II) anthracene-9-carboxylate. Blue circles are measured values at different temperatures and the red curve is theoretically calculated based on eq 1.

At 77 K the reflectance at 510–590 nm decreased, which is the reason why the crystal was green and transparent at the lower temperature. The extra 510 nm band at 300 K was the reason for the thermochromism which produces a brown color at 300 K.

Magnetic Susceptibility. The magnetic susceptibility of copper(II) anthracene-9-carboxylate was measured using a SQUID (Quantum Design, MPM-5s) magnetometer for 2–300 K and that at 300 K was determined by the Gouy method. The temperature dependence of the susceptibility is shown in Figure 5 and it was analyzed on the assumption of coexistence of the singlet and triplet states using the formula below.

$$\chi_A = \frac{N_A g^2 \mu_B{}^2}{kT}\left\{\frac{1}{3+\exp(J/kT)}(1-P)+\frac{1}{4}P\right\}+N_\alpha \quad (1)$$

where J is the Heisenberg exchange integral and P is a correction term showing the presence of a minute amount of mononuclear impurity of less than a few percent and N_α is a temperature-independent paramagnetic term.

The energy J was determined to be $-292\,cm^{-1}$. This value is in good agreement with other copper(II) carboxylates,[13] for instance, $-298\,cm^{-1}$ for cupric acetate monohydrate crystal.[11]

The occupancy of the triplet and singlet states was estimated using J in the following formula

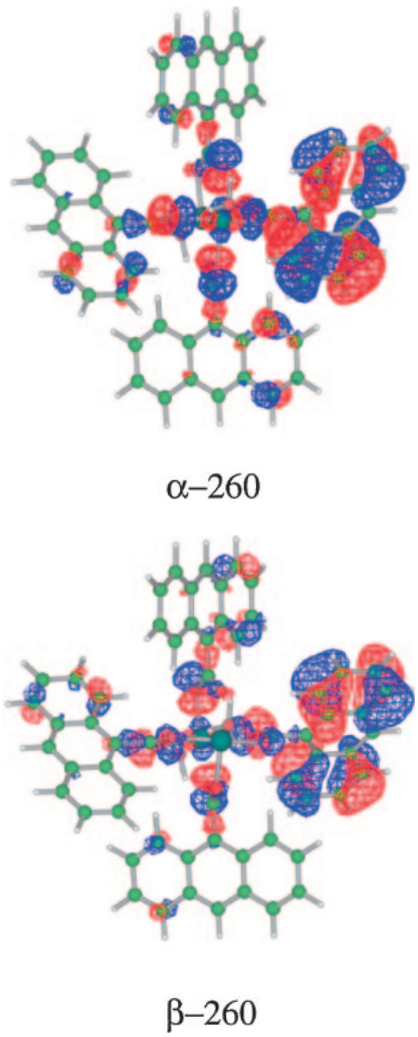

Figure 6. Illustration of MO α-260 and β-260 showing spin polarized Cu $3d_{x^2-y^2}$ orbitals.

$$A = \frac{3\exp(J/kT)}{1+3\exp(J/kT)} \quad (2)$$

At 300 K the occupancy of the triplet state was 42.5% and it dropped to 1.3% at 77 K. Accordingly the extra reflectance peak of the crystal at 510 nm was supposed to be that of the triplet state.

DFT Calculation of Ground State. We performed the DFT calculations on copper(II) anthracene-9-carboxylate two hydrates. as model compounds of the present crystal. The optimized structure was obtained using Gaussian03 program[12] by the UB3LY method with the 6-31G basis set and HOMO–LUMO mixing method. The calculated bond length and dihedral angles are shown in Table 1 together with experimental values. The calculated values were in fairly satisfactory agreement with experimental values; calculated bond lengths were within 0.03 Å and dihedral angles within 10–15° of experimental values. The singlet–triplet energy difference was estimated with the above optimized structure by LANL2DZ basis set, and J was estimated as $-207\,cm^{-1}$ compared to the experimental value of $-292\,cm^{-1}$. Figure 6 shows the characteristics of bonding between the two Cu^{2+} ions for combination

Table 2. Comparison of Experimental and Calculated Absorption Bands and Assignment[a)]

Singlet				Triplet				Assignment
Calculation		Experiment		Calculation		Experiment		
λ	f	λ	f	λ	f	λ	f	
700	0.016	700	0.008	740	0.015	710	0.005	d–d
530	0.11	460	0.007	586	0.11	480	0.027	LMCT
397	0.46	395	0.62	398	0.44	390	0.41	anthracene

a) λ: Wavelength (nm), f: Oscillator strength.

of the α- and β-spin Cu $3d_{x^2-y^2}$ orbitals of MO 260. The HOMO is MO269 and the eight MOs 262–269 are all orbitals extending over the anthracene groups. The combinations of Cu $3d_{x^2-y^2}$ orbitals in MO 260 and 261 are supported by orbitals of the right side anthracene ring as shown in Figure 6. Apparently the bonding between Cu $3d_{x^2-y^2}$ orbitals is by means of superexchange interaction via the carboxylate groups as was found in cupric acetate monohydrate.[11]

Electronic Spectra in EPA Solution and TD-DFT Calculation for the Excited State. The electronic spectra of the molecule in EPA solution were measured with a JASCO V660 spectrophotometer at 300 and 77 K as shown in Figure 7. A red curve was obtained at 300 K and a blue curve at 77 K. Three types of absorption bands can be seen; a weak one at 800–600 nm, medium strength ones at 500 nm for 300 K and 450 nm for 77 K spectra and strong bands at 390–350 nm for both 300 and 77 K. The spectra at 77 K are considered to be those of singlet state, while the spectra at 300 K include both those of singlet and triplet states. TD-DFT calculation was performed with 6-31+G(d) basis for assignment of spectra. The weak band at 700 nm is the d–d transition of the Cu^{2+} ion associated with anthracene carboxylates nonbonding O orbitals, accordingly its intensity is much larger than the usual d–d transition of the free Cu^{2+} ion. The medium intensity band at 500–450 nm is a ligand to metal charge-transfer (LMCT) band. Its position is red-shifted in the triplet state since the energy level of the β-LUMO is lowered and the LMCT bands of triplet state (^{3}LMCT) appears due to the transition from the filled β-MOs to β-LUMO. Parts of the relevant MOs involved for singlet and triplet LMCT bands are shown in Figure 8. It is shown that electrons on MOs extending on anthracene ring transfer to antibonding Cu $3d_{x^2-y^2}$ orbitals. In the 400–350 nm region strong absorption bands due to anthracene chromophore groups were observed. A plot of the calculated results by the GausView program is shown in Figure 7 and the summary of assignments are tabulated in Table 2.

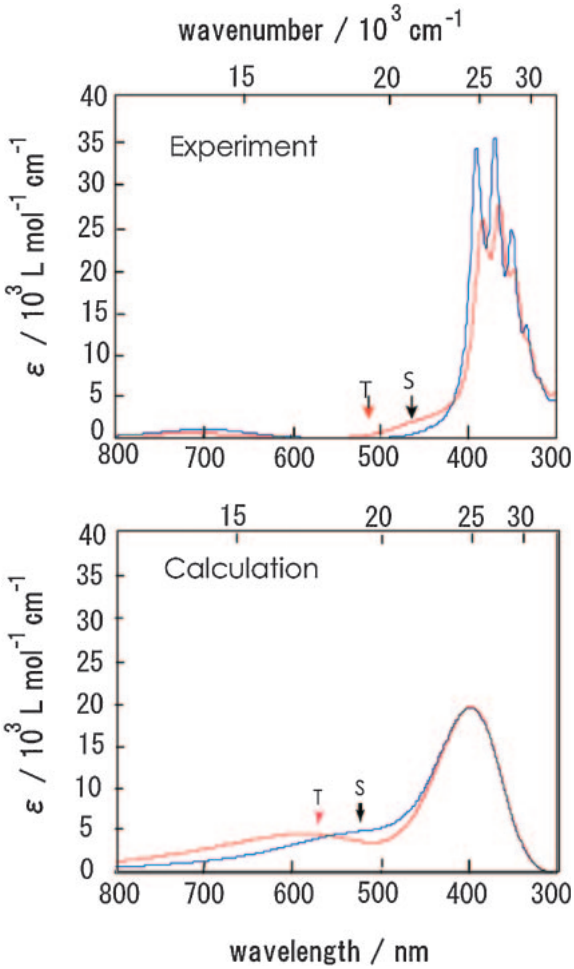

Figure 7. (Top) Electronic absorption spectra of copper(II) anthracene-9-carboxylate in EPA solution at 300 (red curve) and 77 K (blue curve). The position of LMCT bands for triplet and singlet states are shown by arrows. (Bottom) Calculated electronic absorption bands by TD-DFT method. The calculated results are smoothed by GausView program.

Conclusion

The thermochromism of the single crystal of copper(II) anthracene-9-carboxylate is investigated experimentally and theoretically. Conformational change was not found by X-ray crystal structure analysis at 233 and 113 K showing that the thermochromism is not of the structural origin. Magnetic susceptibility measurement for 300–2 K showed coexistence of the triplet and singlet state and the occupancy of triplet state at 300 K was estimated to be 42.5% while it drops to 1.3% at 77 K. Diffuse reflection spectra at 300 and 77 K and molecular spectra in EPA solution at 300 and 77 K showed the triplet band at 510 nm. DFT and TD-DFT calculations were performed to confirm assignment of spectra and magnetic properties. The thermochromism was ascribed to a decrease of occupancy in the triplet state at 300 K due to a drop in temperature. The LMCT band of the triplet state (^{3}LMCT) at 510 nm diminished with a decrease of temperature and this is the reason why the color of the crystal changed from brown to light green.

Theoretical calculations were partly performed at the Research Center for Computational Science, Okazaki, Japan.

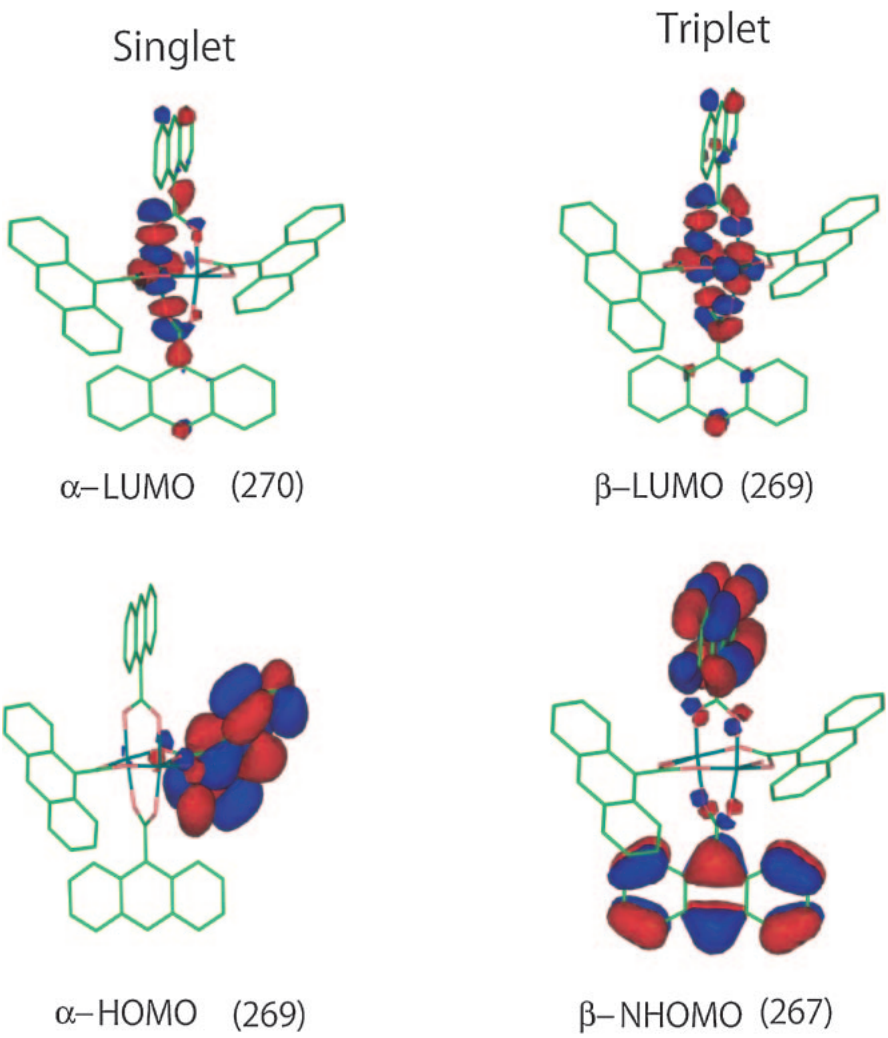

Figure 8. Examples of MOs involved in LMCT bands of singlet and triplet states. The electrons on HOMO, NHOMO, and nearby MOs extended over anthracene ring transfer to vacant orbitals which are antisymmetric combination of two Cu $3d_{x^2-y^2}$ orbitals.

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