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Electronic Structure of *N*,*N*′-Bis(2-aminobenzylidene)ethylenediaminatocopper(II)

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The electronic absorption spectra of *N*,*N*′-bis(2-aminobenzylidene)ethylenediaminatocopper(II) (abbreviated to [Cu(amben)]) were measured in ethanol and in a KBr disk. From these spectral data together with the polarization spectrum in a stretched PVA film, the X-ray photoelectron spectra, and a VESCF-MO-CI calculation, the electronic structure of [Cu(amben)] has been clarified. The reduced polarization spectrum shows that [Cu(amben)] has longer-molecular axis (*y*) polarized bands at 438, 300, 280, 257.7 and 222 nm, and shorter ones (*z*) at 418, 280, 260, 242.5 and 224 nm. The 300 nm band is assigned to an overlap of the calculated $\pi\pi^*_3$ and $\pi\pi^*_4$ transitions, which are charge transfer transitions between the two π-electronic systems localized almost independently on the 2-aminobenzylideneimino groups. The solid-state electronic absorption bands, measured in a KBr disk, of [Cu(amben)] are red-shifted by 2–16 nm, and considerably broadened compared with those in ethanol, indicating that the [Cu(amben)] molecules interact significantly in the solid state. The mechanism of the intermolecular interactions is discussed using the concept of the exciton model. XPS measurements show that the degree of the charge transfer from the ligand to the metal ion in [Cu(amben)] is less than that in *N*,*N*′-disalicylideneethylenediaminatocopper(II) in the ground state.

Recently, metal complexes with organic ligands have attracted much attention from the viewpoints of biological and materials science.[1–10] For instance, manganese(III) complexes with Schiff bases are used as catalysts for the synthesizing selective enantiomers.[9,10]

N,*N*′-disalicylideneethylenediamine (abbreviated to H_2salen) is one of the bridged-type Schiff bases, and easily forms metal complexes.[11–13] A single crystal X-ray diffraction analysis of *N*,*N*′-disalicylideneethylenediaminatocopper(II) (abbreviated to [Cu(salen)]) has already been performed; [Cu(salen)] forms a dimer through two Cu–O^- bonds.[14] In a previous paper, we described the assignment of the electronic bands of [Cu(salen)] based on the polarization spectrum with the aid of the stretched polymer film technique and a MO calculation.[15] The 354, 273.0 and 230.4 nm bands of [Cu(salen)] in the stretched PVA film were assigned to the calculated $\pi\pi^*_2$, $\pi\pi^*_4$ and $\pi\pi^*_7$ transitions, respectively, and the ≈ 250 nm band to the CT transition between the ligand and the metal ion. [Cu(salen)] shows a dd^* band at 565 nm in ethanol.

N,*N*′-bis(2-aminobenzylidene)ethylenediamine (abbreviated to H_2amben) also forms metal complexes easily with transition metal ions.[16–18] The electronic absorption spectra of *N*,*N*′-bis(2-aminobenzylidene)ethylenediaminatocopper(II) (abbreviated to [Cu(amben)]) have been measured in chloroform and pyridine together with the diffused reflection spectrum in the solid state; it has been clarified that the central metal ion takes a square planar structure in solutions and in the solid state.[19] The 417 and 253 nm bands observed in chloroform are assigned to the $\pi\pi^*$ transitions, the 679.8 nm band to the dd^* transition, and the 460 nm band to the LMCT transition (charge transfer transition from ligand to metal, πd^*).[21] These electronic transition properties and the ESR spectrum also show that the central Cu(II) takes a square planar structure. According to a single crystal X-ray diffraction analysis, [Cu(amben)] exists as a monomeric form and the Cu(II) takes a square planar structure.[22] In addition to the above studies, there are several papers on [Cu(amben)].[23–29] However, few papers have been published on the complete assignment of the electronic bands as well as the whole electronic structure of [Cu(amben)].

In the present investigation, we measured the electronic absorption spectrum in ethanol, the solid-state absorption spectrum in the KBr disk, the polarized absorption spectrum in the stretched PVA film, and an X-ray photoelectron spectrum for [Cu(amben)]. From the above spectral data together with MO calculations based on the VESCF-MO-CI approximation,[30] we clarified the electronic structure and the nature of the electronic transitions of [Cu(amben)].

Experimental

Materials. [Cu(amben)]: 1.0 g of H_2amben (Tokyo Kasei) was dissolved in 60 mL of ethanol at 70 °C, to which 2.0 g of $CuSO_4$ dissolved in 25 mL of aqueous ammonia was added; the mixed solution was refluxed for 1 h. The obtained brown powder was recrystallized twice from ethanol, and brown plates were obtained (yield: 68%).[16]

Ethanol (Wako, S Grade) was used as received. PVA films were prepared by an already described method.[31]

Measurements. The electronic absorption spectra were measured with a Shimadzu UV-3101PC spectrophotometer. The polar-

ized absorption spectra were recorded on the above spectrophotometer equipped with a Rochon type polarizer. The X-ray photoelectron spectra (XPS) were recorded on a Shimadzu ESCA-K1, in which the binding energies were calibrated using Au powders as an internal standard (Au $4f_{7/2}$ = 83.8 eV).

MO Calculation

In MO calculations, a VESCF-MO-CI method was used,[30] in which one-center electron repulsion integrals, (rr|rr)'s, were evaluated using the Paoloni equation,[32]

$$(rr|rr) = 3.294\, Z_r, \quad (1)$$

where Z_r is the effective nuclear charge of atom r. The two-center electron repulsion and resonance integrals were evaluated by the Nishimoto–Mataga[33] and the Nishimoto–Forster[34,35] equations, respectively. The valence state ionization potentials, I_C and I_{N^-}, of C and N^- were calculated at every SCF MO calculation, using the following equations:

$$I_C = 3.685\, Z_C{}^2 - 10.008\, Z_C + 4.823, \quad (2)$$

$$I_{N^-\rightarrow N^+} = I_{N^-\rightarrow N} + (N^-N^-|N^-N^-), \quad (3)$$

$$I_{N^-\rightarrow N} = 4.525\, Z_{N^-}{}^2 - 19.140\, Z_{N^-} + 18.071. \quad (4)$$

Here, $I_{N^-\rightarrow N}$ and $I_{N^-\rightarrow N^+}$ are the first and the second ionization potentials of N^-, respectively.[36] The value of Z_r was obtained using

$$Z_r = N_r - S_r - 0.35(\sigma_r + P_{rr}), \quad (5)$$

where N_r is the atomic number of atom r, S_r is a constant determined from the Slater rule, σ_r is the number of σ electrons (e.g. 3 for C and 4 for N^-), and P_{rr} is the π-electron density. The effect of the central metal ion on the π-electronic systems was considered to be a point charge (0.4 e).

Results and Discussion

Electronic Absorption Spectra. Several papers have been published on the syntheses and physicochemical properties for metal complexes with H_2amben,[16–22] but to our knowledge few papers concern the nature of the electronic structure or the electronic transitions. Figure 1 shows the electronic absorption and the solid-state absorption spectra of [Cu(amben)] in ethanol and in the KBr disk together with that of [Cu(salen)] measured in ethanol. [Cu(amben)] shows electronic absorption bands at 679, 460 (shoulder), 414.5, 394 (shoulder), 295.2, 280 (shoulder) and 254.8 nm in ethanol. It is obvious that the 679 nm band (molar absorptivity 205) is due to a dd* transition. The electronic absorption bands of [Cu(salen)] are at 565, ≈ 384 (shoulder), 359, 273.0, 246 (shoulder) and 230.0 nm in ethanol.[15] The band of [Cu(salen)], assigned to the dd* transition, is largely blue-shifted compared with that of [Cu(amben)], and appears at 565 nm. The transition energy of the dd* transition is largely dependent on the splitting pattern of the d orbitals due to the ligand field. The above experimental results show that the extent of the interactions between the metal and the ligand in [Cu(amben)] is considerably small compared with that in [Cu(salen)]. The 414.5 nm band of [Cu(amben)] may correspond to the 359 nm band of [Cu(salen)].

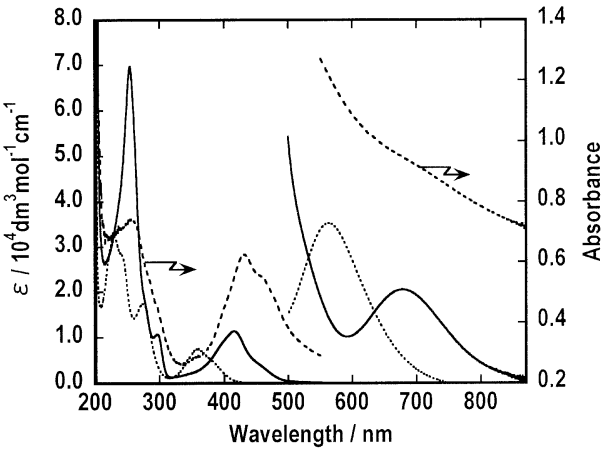


Fig. 1. The absorption spectra of [Cu(amben)] (solid line) and [Cu(salen)] (dotted line) in ethanol and the solid-state absorption spectrum of [Cu(amben)] in the KBr disk (broken line).

In order to know the polarization directions of the bands of [Cu(amben)], a polarized absorption spectrum was measured in the stretched PVA film, as shown in Fig. 2. In this figure, the $D_{\parallel}$ and $D_{\perp}$ curves mean the absorption spectra measured with light beams polarized parallel to and perpendicular to the stretched direction of the PVA film, respectively. R_s is the stretched ratio of the PVA film, and R_d is a ratio of $D_{\parallel}$ and $D_{\perp}$ ($R_d = D_{\parallel} / D_{\perp}$). The 414.5, 295.2, 280 and 254.8 nm bands in ethanol correspond to the 416, 298, 280 and 257.5 nm bands in the PVA film. Moreover, in the PVA film additional bands which can not be apparently observed in ethanol are seen at ≈ 450, 243 and 222 nm. The 298 and 257.5 nm bands with maxima in the R_d curve are found to be polarized along the longer-molecular axis (y). The R_d curve is heightened in the lower energy side of the 416 nm band, clearly indicating the existence of a longer-molecular axis polarized band at around 450 nm. The 416, 280, 243 and 222 nm bands with lower R_d

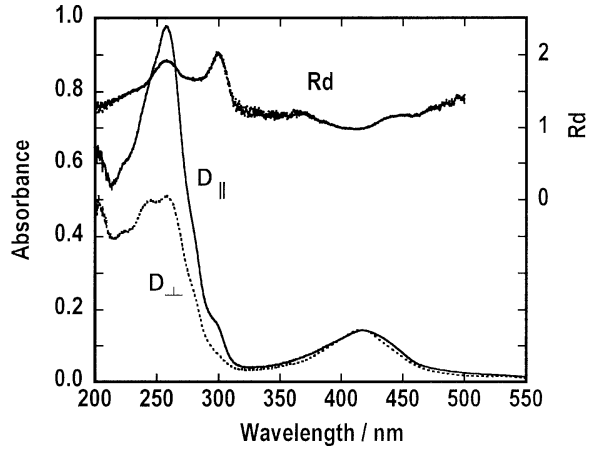


Fig. 2. The polarized absorption spectrum of [Cu(amben)] in the stretched PVA film at room temperature (R_s = 7.9).

values are found to be polarized along the shorter-molecular axis (z). The intensity of the dd* transition is too weak to be observed in the PVA film.

A single crystal X-ray diffraction analysis shows that [Cu(amben)] takes an almost planar structure,[22] and that the [Cu(amben)] molecule belongs approximately to a C_{2v} point group. Thus, the absorption spectrum (D) measured in the isotropic (unstretched) PVA film was divided into two component spectra (D_y and D_z) polarized along the y- and z-axis using the R_d and R_s; i.e., a reduced polarization spectrum was obtained (Fig. 3).[37] The reduced polarization spectrum clearly indicates that [Cu(amben)] shows the y-axis polarized absorption bands at 438, 300, 280 (shoulder), 257.7 and 222 nm, and the z-axis ones at 418, 280 (shoulder), 260, 242.5 and 224 nm.

The solid-state electronic absorption spectrum of [Cu(amben)] measured in the KBr disk is shown in Fig. 1. [Cu(amben)] shows the electronic absorption bands at 462 (shoulder), 431.0, 298 (shoulder), 285 (shoulder) and 258 nm in the KBr disk, which correspond to the bands at 460, 414.5, 295.2, 280 and 254.8 nm in ethanol, respectively. However, each band in the solid state is largely red-shifted compared with that in ethanol, e.g. the 254.8 nm band in ethanol is shifted to 258 nm, and greatly weakened in the solid state. The shoulder at ≈700 nm may be due to a dd* transition of the solid-state [Cu(amben)]. The above-mentioned large spectral change indicates that [Cu(amben)] molecules significantly interact with each other in the solid state. According to an X-ray diffraction analysis, the single crystal of [Cu(amben)] belongs to the space group $P2_12_12_1$ (#19),[22] i.e., [Cu(amben)] takes a column structure

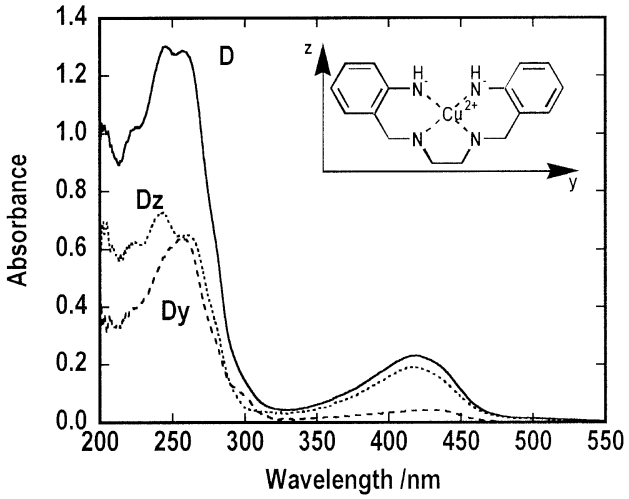


Fig. 3. The reduced polarization spectrum of [Cu(amben)].

along the b-axis, and the neighboring two molecules are arranged as a head-to-tail type and so as to interact with each other through the π-electronic systems of the benzene skeletons. The spectral pattern of the solid-state [Cu(amben)] is in harmony with the results of the X-ray diffraction analysis. According to the concept of the exciton model,[38,39] the energy level of the monomer is split into two levels by a intermolecular interaction between two adjacent molecules, in which three interacting patterns, sandwich (1), oblique sandwich and oblique head-to-tail (2), and head-to-tail (3) types, can be considered (Fig. 4).

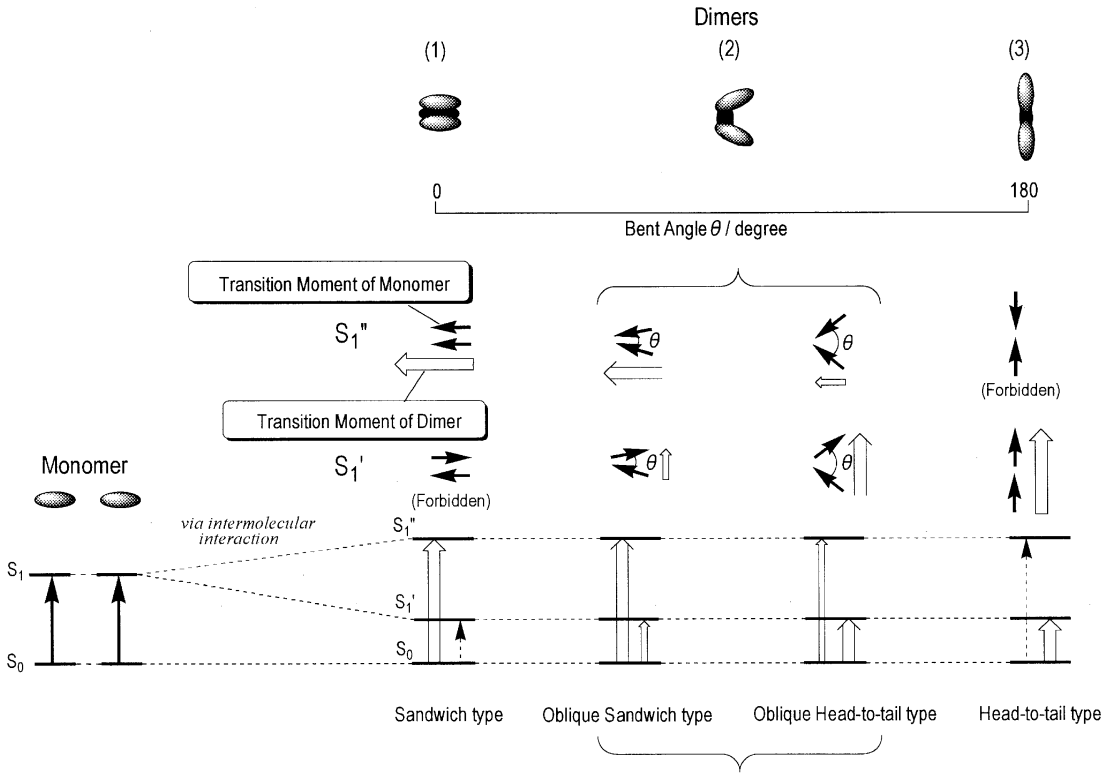


Fig. 4. The energy level splitting patterns obtained from the exciton interaction model.

In type (1) the higher energy transition is allowed and the lower one is forbidden, in type (2) both higher and lower transitions are allowed, and in type (3) the higher energy transition is forbidden and the lower one is allowed. Both the 460 and 414.5 nm bands in ethanol are red-shifted in the KBr disk, suggesting that the type of intermolecular interaction is head-to-tail or oblique head-to-tail. This speculation is in harmony with the molecular arrangement in the crystal obtained from an X-ray diffraction analysis.

X-ray Photoelectron Spectrum. Figure 5 shows the Cu 2p and N 1s X-ray photoelectron bands of [Cu(amben)] and [Cu(salen)]; the results are summarized in Table 1. The Cu $2p_{3/2}$ and Cu $2p_{1/2}$ bands of [Cu(amben)] are observed at 933.3 and 953.2 eV. These bands appear at a higher energy side by ca. 0.5 eV compared with the corresponding bands (932.8 and 952.7 eV) of [Cu(salen)]. As a rule, the Cu 2p band of a Cu(II) complex with an organic ligand is observed at the lower energy side as interactions between Cu(II) and the ligand are strengthened.[20] Thus, the above XPS data show that Cu(II) interacts more weakly with the ligand amben than with salen.

The N 1s bands of [Cu(amben)] and [Cu(salen)] are at 396.6 and 397.3 eV, respectively. The N 1s band of [Cu(amben)] is considerably broad compared with that of [Cu(salen)], i.e., the full width at half maximum (fwhm) of the former is 2.24 and that of the latter 1.61 eV. These experimental results are in harmony with the deduction derived from the molecular structures of [Cu(amben)] and [Cu(salen)], which have two and one kinds of N atoms, respectively. The lengths of the four C–N bonds in [Cu(amben)] are 1.26(2) (C–N$^-$), 1.30(2) (C–N$^{-\prime}$), 1.28(2) (C=N) and 1.27(2) (C=N′) Å, and those of the four N–Cu bonds are 1.97(1) (N$^-$–Cu), 1.88(1) (N$^{-\prime}$–Cu), 1.96(1) (N–Cu) and 1.95(1) (N′–Cu) Å.[22] The C–N single bond lengths are considerably shortened compared with an ordinary C–N single bond (1.39 Å).[40] This suggests that the electron on the negatively charged nitrogen atom of the HN$^-$ group migrates considerably to the azomethine group, following the resonance (Scheme 1). In fact, according to the VESCF-MO-CI calculation, the π-electron densities of the nitrogen atoms of the HN$^-$ and azomethine groups are 1.7505 and 1.2503, respectively. The N 1s band of [Cu(amben)] can be divided into two bands with band maxima at 396.3 and 397.3 eV, assuming a Gaussian distribution. Thus, the 396.3 eV band is assigned to the ionization of the HN$^-$ group and the 397.3 eV band of the azomethine group.

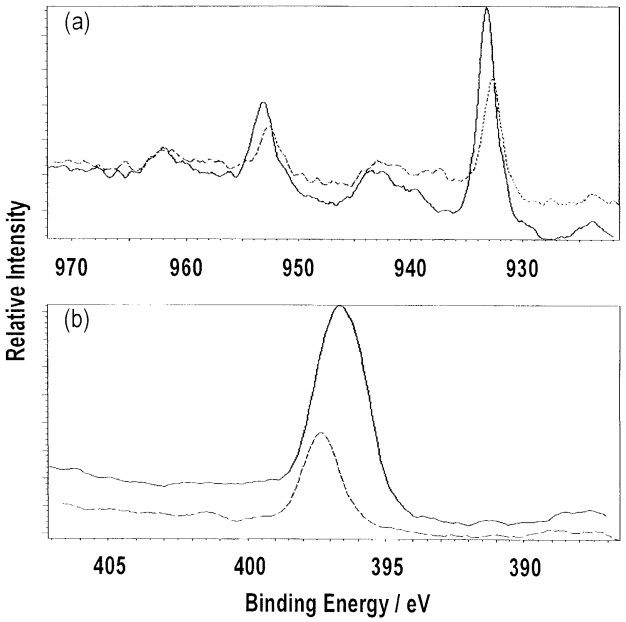
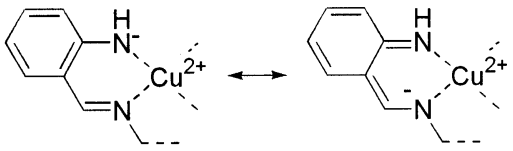


Fig. 5. The Cu 2p (a) and N 1s (b) XPS bands of [Cu(amben)] (solid line) and [Cu(salen)] (broken line).

Assignments of the Electronic Absorption Bands. It is very difficult to clarify the origins of the electronic transitions without the aid of MO calculations. Hitherto, many kinds of MO approximations have been proposed, but few MO methods reproducing the electronic absorption spectra of metal complexes with organic ligands are available. Thus, in the present MO calculation, a point charge approximation was adopted,[41] i.e., the effects of the central metal ion on the π-electronic systems of ligand moieties were taken into account as a point charge in the present VESCF-MO-CI calculation.

Table 2 shows the results of the VESCF-MO-CI calculation compared with the observation. The reduced polarization spectrum (Fig. 3) indicates that [Cu(amben)] shows longer-axis (*y*) polarized bands at 438, 300, 280, 257.7 and 222 nm, and shorter-axis (*z*) polarized bands at 418, 280, 260, 242.5 and 224 nm. The calculated transition energies, intensities and polarization directions well reproduce the observed results; the observed 438 nm band is assigned to the calculated $\pi\pi^*_1$ transition (*y*), the 418 nm band to the $\pi\pi^*_2$ (*z*), the 300 nm band to an overlap of the $\pi\pi^*_3$ and $\pi\pi^*_4$ (accidentally degenerated), the 280 nm band to an overlap of the $\pi\pi^*_5$ and $\pi\pi^*_6$, the 260 nm band to $\pi\pi^*_8$, the 257.7 nm band to an overlap of the $\pi\pi^*_7$ and $\pi\pi^*_9$, and the 242.5 nm band to the $\pi\pi^*_{10}$.

The following Eq. 6 show the excited state wavefunctions



Scheme 1.

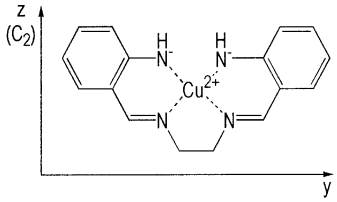
Table 1. The Cu 2p and N 1s XPS Bands of [Cu(amben)] and [Cu(salen)]

Compound	Cu $2p_{3/2}$/eV		Cu $2p_{1/2}$/eV		N 1s/eV
	Main band	Shake up band	Main band	Shake up band	Main band (fwhm)
[Cu(amben)]	933.3	939.5, 943.3	953.2	957.6, 962.0	396.6 (2.24)
[Cu(salen)]	932.8	937.6, 942.6	952.7	957.3, 961.5	397.3 (1.61)

Table 2. The Calculated and Observed Results for $\pi\pi^*$ Transitions of [Cu(amben)]

$\pi\pi^*_n$	Transition energy/nm		Intensity		Polarization direction	
	Calcd	Obsd[a)]	Calcd[b)]	Obsd[c)]	Calcd[d)]	Obsd
$\pi\pi^*_1$	417.9	438	0.00000	0.065	*y*	*y*
$\pi\pi^*_2$	399.2	418	0.31376	0.295	*z*	*z*
$\pi\pi^*_3$	299.5	300	forbidden	0.143		y
$\pi\pi^*_4$	299.5		forbidden			
$\pi\pi^*_5$	296.1	280	0.05186	–	*y*	*z*
$\pi\pi^*_6$	289.8		0.08075		*z*	
$\pi\pi^*_7$	258.3		0.67923		*y*	
$\pi\pi^*_8$	255.7	260	0.03796	1.011	*z*	
$\pi\pi^*_9$	249.5	257.7	1.09539	1.000	*y*	*y*
$\pi\pi^*_{10}$	238.0	242.5	0.31289	1.134	*z*	*z*
$\pi\pi^*_{11}$	217.0		forbidden			
$\pi\pi^*_{12}$	217.0		forbidden			
$\pi\pi^*_{13}$	216.2		0.52156		*y*	
$\pi\pi^*_{14}$	213.2		0.00905		*z*	
$\pi\pi^*_{15}$	210.0		forbidden			
$\pi\pi^*_{16}$	210.0		forbidden			

a) The reduced polarization spectrum. b) Oscillator strength. c) Observed relative intensity with respect to the 257.7 nm band. d) *z*: The C_2 axis; *y*: Perpendicular to the C_2 axis.



Ψ_n for [Cu(amben)]:

$$\Psi_1 = -0.6944\chi_{9,11} - 0.6944\chi_{10,12} + \cdots$$
$$\Psi_2 = 0.6873\chi_{9,11} - 0.6873\chi_{10,12} + \cdots$$
$$\Psi_3 = -0.9857\chi_{10,11} + \cdots$$
$$\Psi_4 = 0.9857\chi_{9,12} + \cdots$$
$$\Psi_5 = 0.4905\chi_{7,11} - 0.4905\chi_{8,12} + 0.4218\chi_{9,13} - 0.4218\chi_{10,14} + \cdots$$
$$\Psi_6 = 0.4618\chi_{7,11} + 0.4618\chi_{8,12} + 0.4476\chi_{9,13} + 0.4476\chi_{10,14} + \cdots$$
$$\Psi_7 = -0.4753\chi_{7,11} + 0.4753\chi_{8,12} - 0.3791\chi_{9,15} + 0.3791\chi_{10,16} + 0.3032\chi_{9,13} - 0.3032\chi_{10,14} + \cdots$$
$$\Psi_8 = -0.5197\chi_{9,15} - 0.5197\chi_{10,16} - 0.3854\chi_{7,11} - 0.3854\chi_{8,12} + \cdots \quad (6)$$
$$\Psi_9 = 0.4689\chi_{9,13} - 0.4689\chi_{10,14} + 0.4022\chi_{9,15} - 0.4022\chi_{10,16} + \cdots$$
$$\Psi_{10} = 0.5169\chi_{9,13} + 0.5169\chi_{10,14} - 0.3141\chi_{7,11} - 0.3141\chi_{8,12} + \cdots$$
$$\Psi_{11} = 0.9935\chi_{8,11} + \cdots$$
$$\Psi_{12} = 0.9935\chi_{7,12} + \cdots$$
$$\Psi_{13} = -0.4823\chi_{5,11} + 0.4823\chi_{6,12} - 0.3683\chi_{9,15} + 0.3683\chi_{10,16} - 0.3200\chi_{7,13} - 0.3200\chi_{8,14} + \cdots$$
$$\Psi_{14} = 0.4624\chi_{5,11} + 0.4624\chi_{6,12} + 0.3815\chi_{9,15} + 0.3815\chi_{10,16} + \cdots$$
$$\Psi_{15} = -0.9909\chi_{10,13} + \cdots$$
$$\Psi_{16} = 0.9909\chi_{9,14} + \cdots$$

Here, $\chi_{i,j}$ is a configuration wavefunction corresponding to one-electron excitation from the occupied orbital ϕ_i to the unoccupied orbital ϕ_j. The MO's contributing mainly to Ψ_n are shown diagrammatically in Fig. 6. To Ψ_1 (or Ψ_2) corresponding to the observed 438 nm band (or 418 nm band), $\chi_{9,11}$ and $\chi_{10,12}$ contribute by 48.2% (or 47.2%) each. As can be seen from the features of ϕ_9, ϕ_{10}, ϕ_{11} and ϕ_{12} shown in Fig. 6, the observed 438 and 418 nm bands can be regarded as intramolecular CT transitions from the HN^- group to the azomethine group in the same 2-aminobenzylideneimino moiety. The 382 and 354 nm bands observed in a PVA film of [Cu(salen)] corresponding to the 438 and 418 nm bands of [Cu(amben)] are also interpreted as an intramolecular CT transition from the oxide group to the azomethine group.[15] The main contributors of Ψ_3 and Ψ_4 for [Cu(amben)] are $\chi_{10,11}$ and $\chi_{9,12}$, respectively, and these two configuration wavefunctions correspond to intramolecular charge transfer excitations between the two π-electronic systems separated by the ethylene group. Thus, the 300 nm band ($\pi\pi^*_3$ and $\pi\pi^*_4$ transitions) can be considered to be an intramolecular CT (LLCT) transition between the two π-electronic systems localized separately on the two 2-aminobenzylideneimino moieties. In the case of [Cu(salen)], a similar LLCT band was also observed at ≈250 nm in a stretched PVA film.[15]

Conclusion

The electronic absorption spectra of [Cu(amben)] were measured in ethanol and in the solid state, together with the polarized absorption spectrum in a stretched PVA film and the X-ray photoelectron spectrum. From these experimental results and VESCF-MO-CI calculation, the nature of the electronic transitions and the electronic structure of [Cu(amben)] have been elucidated. The reduced polarization spectrum for [Cu(am-

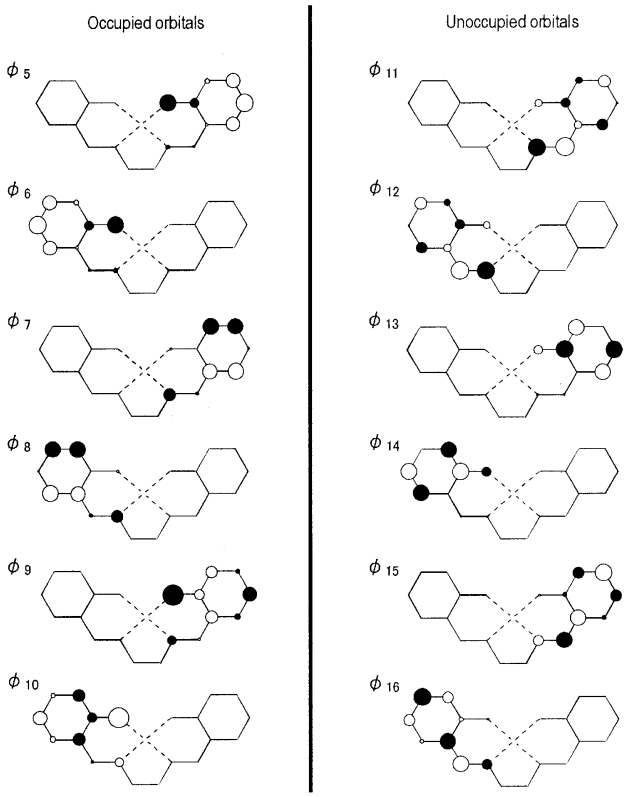


Fig. 6. Diagrammatic representations of MO's for [Cu(amben)].

ben)] shows that the longer-molecular axis (y) polarized bands are at 438, 300, 280 (shoulder), 257.7 and 222 nm, and the shorter-molecular axis (z) polarized ones at 418, 280 (shoulder), 260, 242.5 and 224 nm. The 438 and 418 nm bands are assigned to the $\pi\pi^*_1$ and $\pi\pi^*_2$ transitions, which are regarded as intramolecular CT transitions from the HN^- group to the azomethine group. The 300 nm band is interpreted as an intramolecular CT transition between the two π-electronic systems separated by an ethylene group. The dd* transition of [Cu(amben)] appears at 679 nm in ethanol. The solid-state electronic absorption bands of [Cu(amben)] observed in the KBr disk are shifted to a lower energy side and broadened compared with those in ethanol. The dd* transition energy of [Cu(amben)] is lower than that of [Cu(salen)], and the XPS Cu 2p binding energy of [Cu(amben)] is higher, indicating that the Cu(II) interacts with the ligand amben more weakly than Cu(II) does with salen.

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References

1 M. B. Ferrari, G. G. Fava, and C. Pelizzi, *Acta Crystallogr*, **B32**, 901 (1976).

2 R. V. Singh and J. P. Tandon, *J. Inorg. Nucl. Chem.*, **40**, 2065 (1978).

3 E. G. Samsel, K. Srinivasan, and J. K. Kochi, *J. Am. Chem. Soc.*, **107**, 7606 (1985).

4 P. S. Dixit and K. Srinivasan, *Inorg. Chem.*, **27**, 4507 (1988).

5 Y. Sreenivasulu and K. H. Reddy, *J. Indian Chem. Soc.*, **71**, 41 (1994).

6 D. J. Gravert and J. H. Griffin, *Inorg. Chem.*, **35**, 4837 (1996).

7 M. S. Sigman and E. N. Jacobsen, *J. Am. Chem. Soc.*, **120**, 5315 (1998).

8 F. Sakamoto, T. Sumiya, M. Fujita, T. Tada, X. S. Tan, E. Suzuki, I. Okura, and Y. Fujii, *Chem. Lett.*, **11**, 1127 (1998).

9 T. Katsuki, *J. Mol. Catal. A*, **113**, 87 (1996).

10 Y. N. Ito and T. Katsuki, *Bull. Chem. Soc. Jpn.*, **72**, 603 (1999).

11 C. S. Marvel, S. A. Aspey, and E. A. Dudley, *J. Am. Chem. Soc.*, **78**, 4905 (1956).

12 C. Huilan, H. Deyan, L. Tian, Y. Hong, J. Chen, P. Zheng, and C. Chen, *Inorg. Chem.*, **35**, 1502 (1996).

13 D. A. Atwood, J. A. Jegier, and D. Rutherford, *Inorg. Chem.*, **35**, 63 (1996).

14 D. Hall and T. N. Waters, *J. Chem. Soc.*, **1960**, 2644.

15 T. Hoshi, Y. Inomaki, M. Wada, Y. Yamada, J. Okubo, M. Kobayashi, and H. Inoue, *Ber. Bunsenges. Phys. Chem.*, **98**, 585 (1994).

16 P. Pfeiffer, T. Hesse, H. Pfitzner, W. Scholl, and H. H. Thielert, *J. Prakt. Chem.*, **149**, 217 (1937).

17 M. Green and P. A. Tasker, *J. Chem. Soc., A*, **1970**, 2531.

18 M. Green and P. A. Tasker, *J. Chem. Soc., A*, **1970**, 3105.

19 B. M. Higson and E. D. McKenzie, *J. Chem. Soc.*, **1972**, 269.

20 J. G. Dillard and L. T. Taylor, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 455 (1974).

21 G. A. Bowmaker, T. N. Waters, and P. E. Wright, *J. Chem. Soc., Dalton Trans.*, **1975**, 867.

22 G. Brewer, J. Jasinski, W. Mahany, L. May, and S. Prytkov, *Inorg. Chim. Acta*, **232**, 183 (1995).

23 M. Green and P. A. Tasker, *Inorg. Chim. Acta.*, **5**, 65 (1971).

24 A. D. Toy, M. D. Hobday, P. W. D. Boyd, T. D. Smith, and J. R. Pilbrow, *J. Chem. Soc., Dalton Trans.*, **1973**, 1259.

25 W. C. Gilbert, L. T. Taylor, and J. G. Dillard, *J. Am. Chem. Soc.*, **95**, 2477 (1973).

26 V. Malatesta and B. R. McGarvey, *Can. J. Chem.*, **53**, 3971 (1975).

27 M. Iwaizumi, T. Kudo, and S. Kita, *Inorg. Chem.*, **25**, 1546 (1986).

28 G. W. Dillow, I. K. Gregor, and M. Guilhaus, *Org. Mass Spectrom.*, **21**, 151 (1986).

29 A. N. Zakharou, and N. S. Zefirov, *Kinet. Catal.*, **39**, 493 (1998).

30 T. Hoshi, J. Yoshino, and K. Hayashi, *Z. Physik. Chem. Neue Folge*, **83**, 31 (1973).

31 T. Hoshi and Y. Tanizaki, *Z. Phy. Chem.*, **71**, 230 (1970).

32 R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.*, **54**, 757 (1958).

33 N. Mataga and K. Nishimoto, *Z. Phys. Chem. Neue Folge.*, **13**, 140 (1958).

34 K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **3**, 407 (1965).

35 K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **4**, 155 (1966).

36 J. Allinger, T. W. Stuart, and J. C. Tai, *J. Am. Chem. Soc.*, **90**, 2809 (1968).

37 H. Inoue, T. Hoshi, T. Masamoto, J. Shiraishi, and Y.

Tanizaki, *Ber. Bunsenges. Phys. Chem.*, **75**, 441 (1971).
38 M. Kasha, *Rev. Mod. Phys.*, **31**, 162 (1959).
39 J. P. Hernandez, and S. -I. Choi, *J. Chem. Phys.*, **50**, 1524 (1969).
40 "Kagaku Binran the 4th edition," ed by the Chemical Society of Japan, Maruzen, Tokyo (1993).
41 M. Hasegawa, K. Kumagai, M. Terauchi, J. Okubo, and T. Hoshi, *Can. J. Chem.*, submitted in 2001.