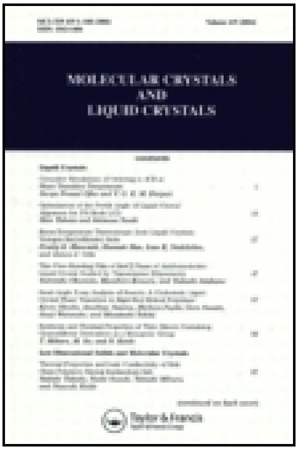

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Electronic Structure of (2,2′-Bipyridine)(Catecholato)Copper(II)

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ELECTRONIC STRUCTURE OF (2,2'-BIPYRIDINE)(CATECHOLATO)COPPER(II)

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Abstract The polarized absorption spectrum of (2,2'-bipyridine)(catecholato)-copper(II) ([Cu(cat)(bpy)]) has been measured in the stretched poly(vinyl alcohol) (PVA) film at room temperature. It is found that the 312, 295 and 215 nm bands of [Cu(cat)(bpy)] are due to transitions localized on the bipyridine (bpy) moiety, and the 306 and 247 nm bands on the catecholate (cat) moiety. The observed 322 nm band can be regarded as an intramolecular interligand CT (LL'CT) transition from cat to bpy. The 207 nm band can be interpreted as superimposition of the two localized excitations cat and bpy, respectively, and LL'CT excitation. This implies that the two π-electronic systems of [Cu(cat)(bpy)], existing almost independently on the two ligands, can interact significantly. The complex [Cu(cat)(bpy)] shows d-d bands at 750, 625 and 550 nm, and intramolecular CT bands between the ligands and metal at 425, 335 and 245 nm.

INTRODUCTION

It is well known that (2,2'-bipyridine)(catecholato)copper(II) ([Cu(cat)(bpy)]), which is one of typical ternary copper(II) complexes, shows very high stability constant.[1-10] Physicochemical properties of [Cu(cat)(bpy)] have been studied by several investigators, but there are few investigations on electronic transitions or electronic structure of the complex.[11, 12] In the present investigation, the polarized absorption spectrum of [Cu(cat)(bpy)] has been measured with the aid of a stretched polymer film technique[13, 14] to determine polarization directions of the electronic bands. From the above experimental results together with MO calculations based on the extended PPP method,[15, 16] which can apply to the metal complexes, electronic structure and nature of electronic transitions of [Cu(cat)(bpy)] have been clarified.

EXPERIMENTAL AND MO CALCULATIONS

The complex [Cu(cat)(bpy)] was synthesized and purified by the method described elsewhere.[5] Stretched poly(vinyl alcohol) (PVA) films containing sample molecules were prepared by a previously described method.[13, 14]

Polarized absorption spectra were recorded on a Shimadzu UV-3101PC spectrophotometer equipped with a Rochon type polarizer. The notations used for the polarization and reduced spectra[13, 17] are as follows: $D_{\parallel}$ and $D_{\perp}$ are optical densities measured with light beams polarized parallel to and perpendicular to the stretching direction of the PVA film, respectively; Rd is the ratio of $D_{\parallel}$ and $D_{\perp}$ (Rd $= D_{\parallel} / D_{\perp}$); Rs is a stretching ratio of the film; D is an optical density in an unstretched PVA sheet; D_Y and D_Z are optical densities, whose transition moments are along the Y (perpendicular to the C_2) and Z (parallel to the C_2) axes, respectively ($D = D_Y + D_Z$).

MO calculations were performed by a modified PPP method, which can apply to the metal complexes, and the details of the method were described in the previous papers.[15, 16]

RESULTS AND DISCUSSION

The polarized absorption spectrum of [Cu(cat)(bpy)] measured in the stretched PVA film is shown in FIGURE 1. In the PVA film, [Cu(cat)(bpy)] shows absorption bands at ~625, ~425, 312, 302, 292, 261, 246, 215 and 210 nm. In the film, guest molecules are usually preferentially oriented in such a manner that the long molecular axes incline towards the stretching direction. However, comparison of experimental and calculated results shows that the short molecular axes of the guest molecules incline preferentially to the stretching direction of the polymer film, i. e., in this case

FIGURE 1 The polarized absorption spectrum of [Cu(cat)(bpy)] in the stretched PVA film; Rs = 8.8.

bipyridine moiety in [Cu(cat)(bpy)] play an important role in the adsorption of the guest molecules. This indicates that electronic bands with low Rd values are polarized along the long molecular axis (C_2 or Z axis), and the bands with high Rd values along the short molecular axis (perpendicular to C_2 or Y axis). The Rd curve shows minima around 425 and 210 nm, and maxima around 625, 312, 302 and 292 nm, indicating that the corresponding bands are polarized along Z and Y axes, respectively. On the basis of the results of the above polarization spectrum, the spectrum measured in an unstretched PVA sheet is divided into the Y and Z polarized compoments,[13, 17] and the results are shown in FIGURE 2. This figure shows that

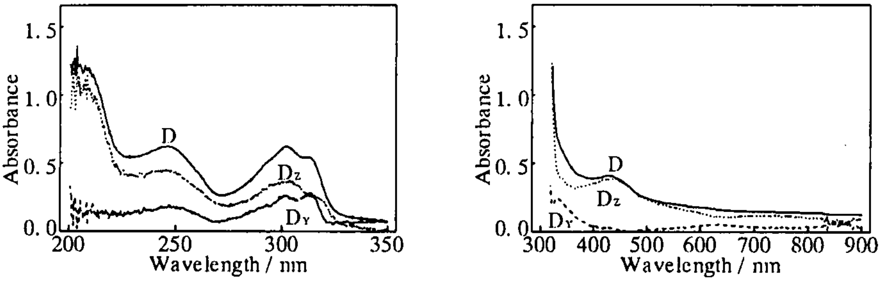


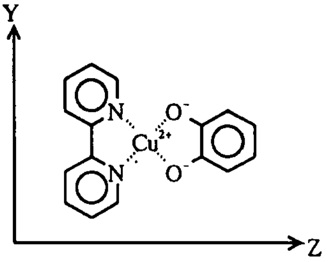
FIGURE 2 The reduce spectrum of [Cu(cat)(bpy)] in the PVA film.

[Cu(cat)(bpy)] has six Y-polarized bands at 625, 335, 312, 302, 292 and 247 nm, and nine Z-polarized bands at 750, 550, 425, 322, 306, 295, 245, 215 and 210 nm. Among these bands, it is clear that the 750, 625 and 550 nm bands are due to d-d transitions. The 302 and 292 nm bands are considered to be vibronic bands, whose progression is $\sim$1000 cm^{-1}, originating at 312 nm. These experimental results are compared with MO calculations in TABLE 1. The Y-polarized 312 and 247 nm bands are assigned to the $\pi\pi^*_2$ and $\pi\pi^*_8$ transitions, respectively. The Z-polarized 322, 306, 295 and 215 nm bands are ascribed to $\pi\pi^*_1$, $\pi\pi^*_3$, $\pi\pi^*_4$ and $\pi\pi^*_{10}$ transitions, respectively, and the 207 nm band is regarded as an overlap of the $\pi\pi^*_{11}$ and $\pi\pi^*_{12}$ transitions. No calculated transitions are found, corresponding to the observed 425, 335 and 245 nm bands. Thus, the bands at 425, 335 and 245 nm may be due to intramolecular CT transitions between the ligands and metal. The band corresponding to the 425nm band of [Cu(cat)(bpy)] also appears with almost the same intensity and transition energy in the spectrum of [Cu(cat)(phen)].[12, 13] In the case of [Cu(cat)(phen)], it has been clarified that the band around 425 nm is due to the intramolecular CT transition between the catecholate (cat) skeleton and copper(II).[16] These facts indicate that the 425 nm band of [Cu(cat)(bpy)] can be regarded as the intramolecular CT transition between

TABLE 1 The calculated and observed results for the $\pi\ \pi^*$ transitions of [Cu(cat)(bpy)].

	Symmetry	Transition energy(nm) calc.	obs.^{a}	Intensity calc.^{b}	obs.^{c}	Polarization direction calc.	obs.
		425^d			0.032		Z
		335^d			0.051		Y
$\pi\ \pi^*_1$	A_1	312.8	322	0.00057	0.136	Z	Z
$\pi\ \pi^*_2$	B_1	305.8	312	0.45610	0.348	Y	Y
$\pi\ \pi^*_3$	A_1	304.7	306	0.03101	0.382	Z	Z
$\pi\ \pi^*_4$	A_1	280.2	295	0.01863	0.368	Z	Z
$\pi\ \pi^*_5$	B_1	258.6		0.00015		Y	
$\pi\ \pi^*_6$	B_1	253.7		0.14573		Y	
$\pi\ \pi^*_7$	B_1	251.3		0.00143		Y	
$\pi\ \pi^*_8$	B_1	251.0	247	0.24579	0.444	Y	Y
			245^d		0.449		Z
$\pi\ \pi^*_9$	A_1	249.3		0.00004		Z	Z
$\pi\ \pi^*_{10}$	A_1	222.2	215	0.07395	0.791	Z	Z
$\pi\ \pi^*_{11}$	A_1	215.0	210	0.56371	1.000	Z	Z
$\pi\ \pi^*_{12}$	A_1	214.6		1.02456		Z	

a: observed in the PVA film
b: oscillator strength
c: relative intensity measured in the PVA film
d: intramolecular CT band between the ligands and metal



cat and copper(II). The total excited state wavefunctions of [Cu(cat)(bpy)] are given below and MO's concerned with the above total wavefunctions are shown diagram-

$$\Psi_1 = -0.9846\,\chi_{11,12} + \cdots$$
$$\Psi_2 = -0.8740\,\chi_{9,12} + \cdots$$
$$\Psi_3 = -0.5807\,\chi_{10,17} + 0.8082\,\chi_{11,16} + \cdots$$
$$\Psi_4 = 0.5747\,\chi_{8,12} - 0.6810\,\chi_{9,13} + \cdots$$
$$\Psi_5 = 0.8971\,\chi_{11,13} + \cdots$$
$$\Psi_6 = 0.4641\,\chi_{7,12} - 0.4074\,\chi_{9,12} - 0.6558\,\chi_{9,14} + \cdots$$
$$\Psi_7 = -0.9051\,\chi_{10,12} + \cdots$$

$$\Psi_8 = -\,0.8795\,\chi_{11,17} + \cdots$$
$$\Psi_9 = -\,0.9762\,\chi_{11,14} + \cdots$$
$$\Psi_{10} = 0.6726\,\chi_{6,12} - 0.3280\,\chi_{7,13} - 0.4316\,\chi_{8,12} + 0.3812\,\chi_{9,13} + \cdots$$
$$\Psi_{11} = 0.2080\,\chi_{8,12} + 0.7977\,\chi_{10,13} - 0.3720\,\chi_{10,17} + \cdots$$
$$\Psi_{12} = 0.2854\,\chi_{8,12} - 0.5798\,\chi_{10,13} - 0.5109\,\chi_{10,17} + \cdots$$

matically in FIGURE 3. Here, $\chi_{i,j}$'s are configurational wavefunctions, corresponding to one electron excitation from the i'th occupied MO (ϕ_i) to the j'th vacant one (ϕ_j). The main contributor to Ψ_1, corresponding to the $\pi\pi^*_1$ transition, is $\chi_{11,12}$.

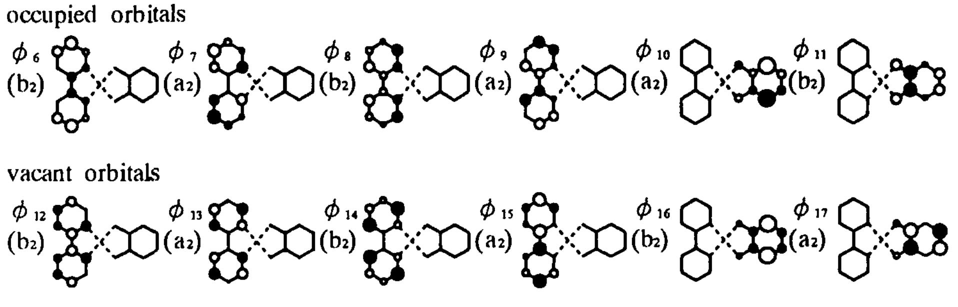


FIGURE 3 Diagrammatic representations of SCF MO's of [Cu(cat)(bpy)].

Molecular orbital ϕ_{11} is the highest occupied orbital (b$_2$) localized on the catecholate (cat) moiety and ϕ_{12} is the lowest unoccupied one (b$_2$) localized on the bipyridine (bpy) moiety, so that the observed 322 nm band can be regarded as $A_1 \leftarrow A_1$ type intramolecular interligand (LL'CT) transition from cat (HOMO) to bpy (LUMO). This implies that the two π-electronic systems, existing almost independently on the two moieties, can interact directly. The main contributor to the state wavefunction Ψ_2 is $\chi_{9,12}$, and ϕ_9 and ϕ_{12} are localized on the bpy moiety. Therefore, the 312 nm band is regarded as a localized electronic transition on the bpy skeleton. Similarly, the 295 and 215nm bands are considered to be localized on the bpy moiety. On the other hand, the main contributors to Ψ_3 are $\chi_{10,17}$ and $\chi_{11,16}$, and that to Ψ_8 is $\chi_{11,17}$. Since ϕ_{10}, ϕ_{11}, ϕ_{16} and ϕ_{17} are localized molecular orbitals on the cat moiety, the 306 and 247 nm bands are due to localized transitions on the cat skeleton. The main contributors to Ψ_{11} and Ψ_{12} are $\chi_{8,12}$, $\chi_{10,13}$ and $\chi_{10,17}$, of which $\chi_{8,12}$ corresponds to one electron excitation in bpy, $\chi_{10,17}$ to excitation in cat and $\chi_{10,13}$ to LL'CT excitation from cat to bpy. This implies that the observed 207 nm band can be interpreted as superimposition of the two localized excitations on cat and bpy, respectively, and LL'CT excitation.

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REFERENCES

1. R. Griesser and H. Sigel, Inorg. Chem., 9, 1238 (1970).
2. P. R. Huber, R. Griesser and H. Sigel, Inorg. Chem., 10, 945 (1971).
3. H. Sigel, P. R. Huber and R. F. Pastemack, Inorg. Chem., 10, 2226 (1971).
4. R. Griesser and H. Sigel, Inorg. Chem., 10, 2229 (1971).
5. F. A. Walkeer, H. Sigel and D. B. McCormick, Inorg. Chem., 11, 2756 (1972).
6. I. P. Mavani, C. R. Jejurkar and P. K. Bhattacharya, J. Indian Chem. Soc., 49, 469 (1972).
7. H. Sigel and B. Prijs, Chimia, 29, 134 (1975).
8. H. Sigel, Angew. Chem. Int. Ed. Engl., 14, 394 (1975).
9. M. S. Mohan, D. Bancroft and E. H. Abbott, Inorg. Chem., 18, 344 (1979).
10. V. Srivastava and H. L. Nigam, J. Indian Chem. Soc., 59, 251 (1982).
11. D. G. Brown, W. J. Hughes and G. Knerr, Inorg. Chim. Acta, 46, 123 (1980).
12. R. Benedix and A. Vogler, Inorg. Chim. Acta, 204, 189 (1993).
13. T. Hoshi and Y. Tanizaki, Z. Phys. Chem. Neue Folge, 71, 230 (1970).
14. T. Hoshi, T. Kawashima, J. Okubo, M. Yamamoto and H. Inoue, J. Chem. Soc. Perkin Trans. II, 1147 (1986).
15. T. Hoshi, Y. Inomaki, M. Wada, Y. Yamada, J. Okubo, M. Kobayashi and H. Inoue, Ber. Bunsenges. Phys. Chem., 98, 585 (1994).
16. Y. Yamada, T. Hoshi and Y. Fukuda, J. Coord. Chem., in press.
17. H. Inoue, T. Hoshi, T. Masamoto, J. Shiraishi and Y. Tanizaki, Ber. Bunsenges. Phys. Chem., 75, 441 (1971).