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Structural evidence for the intramolecular charge-transfer interaction involving an indole ring in ternary copper(II) complexes with L-tryptophan and aromatic diamines

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Abstract

With a view to understanding the precise binding mode and strength of the stacking interaction in the ternary copper(II) complexes comprising an aromatic diamine such as 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) and an aromatic amino acid such as L-phenylalanine, L-tyrosine and L-tryptophan (L-trp), the crystal structure of [Cu(bpy)(L-trp)]ClO_4 and the circular dichroism (CD) and absorption spectra of [Cu(bpy)(L-trp)]ClO_4 and [Cu(phen)(L-trp)]ClO_4 have been investigated. The complex [Cu(bpy)(L-trp)]ClO_4 crystallizes in the monoclinic space group, $P2_1$, with two molecules in a unit cell of dimensions $a=13.022(1)$, $b=7.753(1)$, $c=10.533(1)$ Å, and $\beta=91.18(1)°$. The Cu(II) ion is five-coordinate square-pyramidal, with the two nitrogen atoms of bpy and the nitrogen and oxygen atoms of the amino acid coordinated at the equatorial positions in a slightly distorted square-planar form and the carboxylate oxygen atom of the neighboring molecule at the axial position. The most interesting structural feature of the complex is the existence of the intramolecular stacking interaction between the aromatic rings of L-trp and bpy with the average spacing of 3.67 Å from the vacant axial position. The CD spectra in the d–d region for [Cu(bpy)(L-trp)ClO_4 and [Cu(phen)(L-trp)]ClO_4 in aqueous solution showed a large negative peak at 587 and 598 nm, respectively, and the magnitudes were greatly reduced in dioxane–water, which indicates that the aromatic ring stacking interaction is weakened in a hydrophobic environment. The absorption bands due to the charge transfer (CT) interaction between the indole ring and the aromatic diamine have been observed in the difference spectra in the near ultraviolet region. The strength of the stacking interactions has been demonstrated by the CT band intensity and the distance between the stacked rings to be in the order [Cu(phen)(L-trp)]ClO_4 > [Cu(bpy)(L-trp)]ClO_4 both in solution and in the solid state.

Introduction

The study of non-covalent interactions such as hydrogen bonding, charge transfer (CT), hydrophobic, and electrostatic interactions is one of the paradigms of current biochemical research activities. Many biochemical phenomena are achieved through combination of these non-covalent interactions, which provide the flexibility and specificity required in biochemical processes. Regulation, recognition, transport and catalysis are among the most important aspects of enzymatically specific phenomena.

Aromatic amino acids are reported to contribute to the molecular recognition, stabilization of structure, energy or electron transfer, and so on via the π–π stacking interaction [1–5]. Tryptophan is considered to importantly contribute to the energy or electron transfer [4, 6–8] by virtue of the ability to undergo the strongest π–π interaction due to the side chain indole ring known as the best π-electron donor. We have studied the aromatic ring stacking interaction in ternary transition metal complexes with aromatic diamines and aromatic amino acids on the basis of the stability constants and various spectroscopic methods (electronic absorption, circular dichroism (CD) and NMR) [9–14]. For systems involving transition metal complexes, the interactions may be ligand–ligand interactions around the central metal ion which places the interacting groups in appropriate positions. In addition, metal ions exert electronic effects on the coordinated ligands, making

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direct or through-metal interactions and thus ligand discrimination possible [15–18]. However, the structural evidence for stacking interactions around the central metal ion is rather meager [19–22] probably because of the weakness of such interactions.

We therefore carried out X-ray crystallographic and spectroscopic studies on the copper(II) complexes with L-tryptophan (L-trp) and a diamine (DA = 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen)), [Cu(bpy)(L-trp)]ClO_4 (I) and [Cu(phen)(L-trp)]ClO_4 (II), in order to elucidate the binding mode and strength of the stacking interaction.

Experimental

Preparations of [Cu(bpy)(L-trp)]ClO₄ (I) and [Cu(phen)(L-trp)]ClO₄ (II)

Both ternary complexes were prepared according to the following procedures. $Cu(ClO_4)_2 \cdot 6H_2O$ (5 mmol) and DA (bpy or phen) (5 mmol) dissolved in aqueous methanol were mixed with L-trp (5 mmol) and NaOH (5 mmol) in water. The mixture was heated to complete dissolution, and the crystals which separated on standing at room temperature were collected and recrystallized from aqueous methanol to give the corresponding complexes, [Cu(bpy)(L-trp)]ClO_4 and [Cu(phen)(L-trp)]$ClO_4 \cdot 2.5H_2O$.

Spectral measurements

CD spectra were measured with a JASCO J-40CS spectropolarimeter in quartz cells with a path length of 10 mm. Samples were prepared by dissolving the isolated Cu(II) complexes in water, the concentration being 1 mM (M = mol dm^{-3}) with respect to Cu(II). Absorption spectra were recorded on a Hitachi 330 recording spectrophotometer in quartz cells with a path length of 10 mm. Samples were prepared by dissolving the isolated ternary Cu(II) complexes or their components at neutral pH, and the concentration was adjusted at 10 mM with respect to Cu(II).

X-ray structure determination of [Cu(bpy)(L-trp)]ClO₄ (I)

Single crystals suitable for X-ray diffraction were obtained from an aqueous methanol solution. A greenish blue columnar crystal with dimensions of 0.05 × 0.05 × 0.1 mm was used for collection of intensity data. Diffraction data were collected at 295 K with a Rigaku AFC-5R four-circle diffractometer using graphite-monochromated Cu Kα radiation (λ = 1.54178 Å). Crystal data and details of the parameters associated with data collection are given in Table 1. The unit cell parameters were derived from least-squares refinement of 25 well-centered reflections (40° $\leq 2\theta \leq$ 50°). Data collection showed systematic absences ($k = 2n + 1$ for $0k0$) which uniquely define the monoclinic space group $P2_1$. The intensities of three standard reflections measured every 56 reflections showed no significant variations. Intensity data were collected by the ω–2θ scan technique in the range 1° $\leq 2\theta \leq$ 120°. Lorentz and polarization corrections were applied, but not absorption. For the determination and refinements of the structure, 1723 independent reflections with $|F_o| \geq 3\sigma(F_o)$ were used. The structure was solved by the heavy-atom method and refined by full-matrix least-squarcs method with anisotropic thermal parameters for non-hydrogen atoms. All hydrogen atoms were visible in difference maps and were included as isotropic in the structure factor calculations at the final stage of refinement. Refinement with the weighting scheme $w^{-1} = (\sigma^2(F_o) + (0.023F_o)^2)$ converged at $R = 0.048$ and $R_w = 0.049$. The final electron density maps showed no residual peaks ≥ 3.5 eÅ^{-3} close to the Cu and Cl atoms. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography [23]. All calculations were carried out on a FACOM M 780 computer at the Data Processing Center of Kyoto University by using the program system KPPXRAY [24].

The final positional and isotropic temperature factors of the non-hydrogen atoms are listed in Table 2.

TABLE 1. Crystal data for [Cu(bpy)(L-trp)]ClO_4

Formula	$CuClO_6N_4C_{21}H_{19}$
Formula weight	522.39
Crystal system	monoclinic
Space group	$P2_1$
a (Å)	13.022(1)
b (Å)	7.0753(1)
c (Å)	10.533(1)
β (°)	91.18(1)
V (Å^3)	1063.2
Z	2
ρ (g cm^{-1})	1.632
μ (cm^{-1})	30.23
F(000)	530
Crystal size (mm)	0.05 × 0.05 × 0.10
λ (Cu Kα (Å))	1.54178
2θ limit (°)	120
No. observed reflections ($\lvert F_o\rvert \geq 3\sigma(\lvert F_o\rvert)$)	1636
R	0.048
R_w	0.049

TABLE 2. Final positional parameters and B_{eq} values (Å) for non-hydrogen atoms in [Cu(bpy)(L-trp)]ClO$_4$ (I)[a, b]

Atom	x	y	z	B_{eq}[c]
Cu	0.3818(1)	0.0	0.3725(1)	3.47
Cl	0.1812(2)	0.3023(4)	0.7814(2)	5.71
C(1)	0.2439(5)	0.0017(17)	0.1601(7)	4.00
C(2)	0.1569(6)	0.0239(17)	0.0842(8)	4.79
C(3)	0.0737(7)	0.1057(18)	0.1351(10)	6.37
C(4)	0.0797(7)	0.1698(16)	0.2537(10)	5.71
C(5)	0.1701(6)	0.1496(14)	0.3238(8)	4.70
C(6)	0.3379(6)	−0.0874(12)	0.1150(7)	3.79
C(7)	0.3501(7)	−0.1558(15)	−0.0030(8)	5.03
C(8)	0.4410(8)	−0.2308(16)	−0.0368(8)	5.69
C(9)	0.5207(7)	−0.2319(16)	0.0519(8)	5.53
C(10)	0.5039(7)	−0.1626(15)	0.1714(8)	4.73
C(11)	0.4575(6)	−0.1871(12)	0.5776(7)	3.48
C(12)	0.3695(6)	−0.0799(12)	0.6305(7)	3.74
C(13)	0.2729(6)	−0.2014(15)	0.6470(7)	4.66
C(14)	0.2091(7)	−0.2316(15)	0.5301(8)	4.97
C(15)	0.1123(7)	−0.1634(17)	0.5115(9)	5.76
C(16)	0.1433(8)	−0.3203(15)	0.3366(10)	5.76
C(17)	0.2326(7)	−0.3345(14)	0.4203(9)	4.57
C(18)	0.3142(7)	−0.4364(14)	0.3798(10)	5.53
C(19)	0.3142(8)	−0.5064(21)	0.2618(10)	6.45
C(20)	0.2287(9)	−0.4942(23)	0.1783(10)	7.36
C(21)	0.1440(9)	−0.3988(18)	0.2165(11)	7.55
N(1)	0.2516(5)	0.0671(9)	0.2784(6)	3.56
N(2)	0.4156(5)	−0.0899(10)	0.2039(6)	3.62
N(3)	0.3471(5)	0.0669(10)	0.5488(6)	3.79
N(4)	0.0744(6)	−0.2214(14)	0.3962(8)	6.58
O(1)	0.4809(4)	−0.1576(8)	0.4632(4)	3.39
O(2)	0.5009(4)	−0.2940(8)	0.6486(5)	4.10
O(3)	0.2086(12)	0.4690(23)	0.8291(12)	17.48
O(4)	0.0916(6)	0.2642(20)	0.8380(10)	13.14
O(5)	0.2564(6)	0.1848(13)	0.8171(8)	8.74
O(6)	0.1677(6)	0.3059(18)	0.6498(7)	9.86

[a]Atomic numbering is shown in Fig. 2(a). [b]e.s.d.s are given in parentheses. [c]B_{eq} is the equivalent isotropic temperature factor defined by Hamilton [25].

Results

Crystal structure

The crystal structure is depicted in Fig. 1. The unit cell contains two [Cu(bpy)(L-trp)]$^+$ cations and two well-separated ClO$_4^-$ anions; the shortest Cu...ClO$_4$ distance is 4.72 Å. The central copper ion, five-coordinate, has a distorted square-pyramidal geometry, with the two nitrogen atoms of bpy and the nitrogen and oxygen atoms of L-trp coordinated at the equatorial positions and the carboxylate oxygen of the symmetrically related neighboring [Cu(bpy)(L-trp)]$^+$ cation at the axial position, as shown in Fig. 2. The complex in the crystalline state thus forms an infinite chain structure of [Cu(bpy)(L-trp)]$^+$ cations along a two-fold screw axis (c axis). The three nitrogen and one oxygen atoms are planar to within 0.16 Å and the copper atom deviates by 0.24 Å from

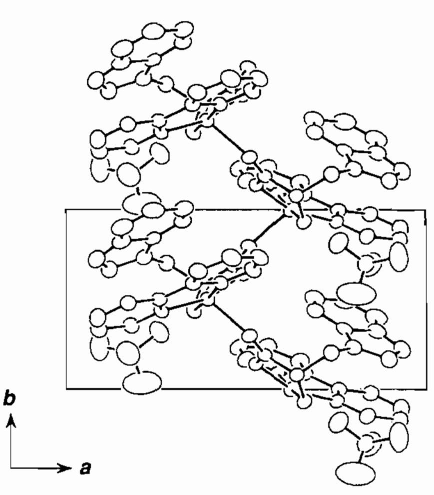

Fig. 1. Crystal structure of [Cu(bpy)(L-trp)]ClO$_4$ (I). The x axis is horizontal to the right, the y axis is almost vertical, and the z axis is about perpendicular to the paper going up to the reader. Hydrogen atoms are omitted.

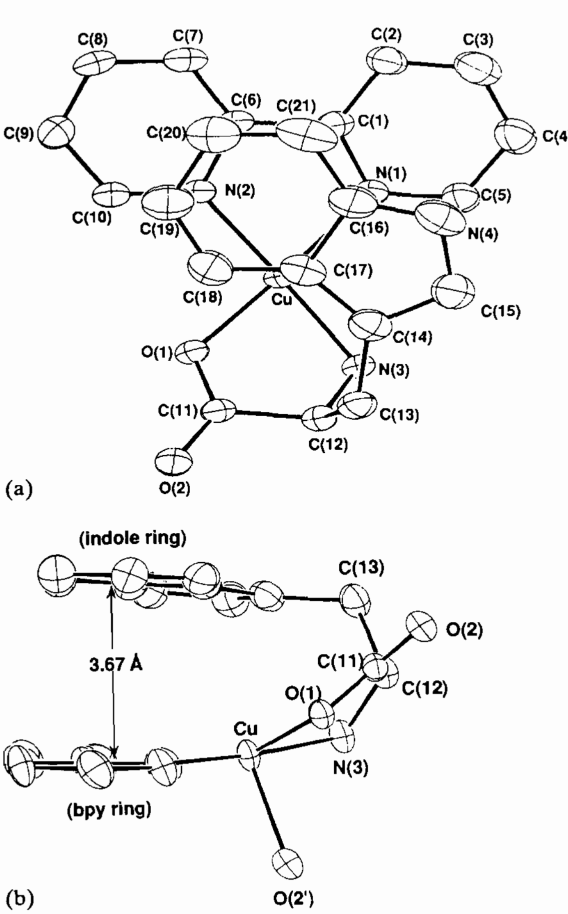

Fig. 2. Diagram showing the stacking interaction between the bpy and indole rings in [Cu(bpy)(L-trp)]ClO$_4$ (I) as viewed upright to the mean plane of the bpy ligand (a) and parallel to the same plane (b). Thermal ellipsoids are drawn at the 50% probability level. The labelling scheme used for the atoms in the molecule is also shown.

the coordination plane (N(1), N(2), N(3) and O(1) atoms) toward the axial oxygen atom.

Bond lengths and angles are presented in Table 3. The equatorial Cu–N and Cu–O bond lengths (Cu–N(1) = 2.015(7), Cu–N(2) = 1.966(7), Cu–N(3) = 1.989(7), and Cu–O(1) = 2.005(5) Å) agree well with those generally found in square-planar Cu(II) complexes [26–28]. The axial Cu–O(2′) bond length, 2.224(6) Å, is slightly longer than the sum of the ionic radii for Cu(II) (0.72 Å) and O^- (1.40 Å) [29] and is shorter than the axial Cu–O bond lengths, 2.262 [19] and 2.301 [28] Å, reported for similar five-coordinate pyramidal Cu(II) complexes. It is still within the range of 2.2–2.9 Å known for the axial Cu–O bond lengths [30], and the O(2′) atom is considered to be coordinately bonded. The opposite site of the axial O(2′) position is occupied by the indole ring of the intramolecular trp group, which is approximately parallel to the bpy plane with the average spacing of 3.67 Å (Fig. 2). There are two close contacts between the Cu(II) ion and the carbon atoms of the indole ring (Cu...C(14) = 3.35 Å and Cu...C(17) = 3.29 Å). Similar intramolecular stacking is also found in complex **II** as previously reported [19, 22].

CD spectra

The ternary systems [Cu(DA)(L-trp)]ClO_4 (DA = bpy or phen) in aqueous solution exhibit a negative maximum due to the d–d transition near 590 nm at neutral pH. The magnitudes of the negative peak are greatly reduced in less polar solvents such as 60 vol.% dioxane–water, indicating that they reflect the intramolecular aromatic ring stacking interaction which is weakened in hydrophobic environments. The spectra and the corresponding data are shown in Fig. 3 and Table 4, respectively. The extent of magnitude decrease is in the order phen < bpy, which is inversely proportional to the number of aromatic rings in DA and suggests that the intramolecular stacking in **II** is less easily affected by solvent polarity than that in **I**.

Absorption spectra

The ternary systems [Cu(DA)(L-trp)]ClO_4 in aqueous solution have a stronger absorption in the near UV region, which is not observed in the spectra of DA, L-trp, Cu(DA)ClO_4 or [Cu(DA)(L-alanine)]ClO_4. The difference spectra obtained from the spectral magnitude observed for the complexes and the sum of the spectral magnitudes for [Cu(DA)(L-alanine)]ClO_4 and L-trp (Fig. 4) gave a weak and broad peak near 320 nm, which is generally ascribed to the charge transfer (CT) between stacked aromatic rings in the complexes [7].

TABLE 3. Interatomic lengths (Å) and angles (°) for [Cu(bpy)(L-trp)]ClO_4 (**I**)[a, b]

Bond	Length
Cu–N(1)	2.015(7)
Cu–N(2)	1.966(7)
Cu–N(3)	1.989(7)
Cu–O(1)	2.005(5)
Cu–O(2′)	2.224(6)
Cl–O(3)	1.429(17)
Cl–O(4)	1.354(9)
Cl–O(5)	1.384(9)
Cl–O(6)	1.394(8)
Cl(1)–C(2)	1.384(11)
C(1)–C(6)	1.492(12)
C(1)–N(1)	1.347(11)
C(2)–C(3)	1.374(14)
C(3)–C(4)	1.345(15)
C(4)–C(5)	1.386(12)
C(5)–N(1)	1.336(11)
C(6)–C(7)	1.364(12)
C(6)–N(2)	1.365(10)
C(7)–C(8)	1.372(14)
C(8)–C(9)	1.382(13)
C(9)–C(10)	1.390(13)
C(10)–N(2)	1.332(12)
C(11)–C(12)	1.530(12)
C(11)–O(1)	1.270(9)
C(11)–O(2)	1.244(10)
C(12)–C(13)	1.584(13)
C(12)–N(3)	1.453(11)
C(13)–C(14)	1.490(11)
C(14)–C(15)	1.377(14)
C(14)–C(17)	1.443(14)
C(15)–N(4)	1.377(13)
C(16)–C(17)	1.449(14)
C(16)–C(21)	1.404(16)
C(16)–N(4)	1.345(14)
C(17)–C(18)	1.398(14)
C(18)–C(19)	1.356(16)
C(19)–C(20)	1.408(15)
C(20)–C(21)	1.394(18)
Bond	Angle
N(1)–Cu–N(2)	81.3(3)
N(1)–Cu–N(3)	100.8(3)
N(1)–Cu–O(1)	156.7(3)
N(2)–Cu–N(3)	174.3(3)
N(2)–Cu–O(1)	93.5(2)
N(3)–Cu–O(1)	82.6(2)
Cu–O(2′)–C(11′)	136.3(5)
O(2′)–Cu–N(1)	109.8(2)
O(2′)–Cu–N(2)	89.9(3)
O(2′)–Cu–N(3)	94.3(3)
O(2′)–Cu–O(1)	92.8(2)
O(3)–Cl–O(4)	104.7(9)
O(3)–Cl–O(5)	109.2(7)
O(3)–Cl–O(6)	110.9(8)
O(4)–Cl–O(5)	110.4(7)
O(4)–Cl–O(6)	110.5(6)
O(5)–Cl–O(6)	110.9(6)

(*continued*)

TABLE 3. (*continued*)

Bond	Angle
C(2)–C(1)–C(6)	122.8(8)
C(2)–C(1)–N(1)	122.1(8)
C(6)–C(1)–N(1)	115.0(6)
C(1)–C(2)–C(3)	118.3(9)
C(2)–C(3)–C(4)	120.1(9)
C(3)–C(4)–C(5)	119.1(9)
C(4)–C(5)–N(1)	122.4(8)
C(1)–C(6)–C(7)	125.6(7)
C(1)–C(6)–N(2)	112.9(7)
C(7)–C(6)–N(2)	121.4(8)
C(6)–C(7)–C(8)	121.2(8)
C(7)–C(8)–C(9)	117.8(9)
C(8)–C(9)–C(10)	118.7(9)
C(9)–C(10)–N(2)	123.3(8)
C(12)–C(11)–O(1)	116.4(7)
C(12)–C(11)–O(2)	118.5(7)
O(1)–C(11)–O(2)	125.1(8)
C(11)–C(12)–C(13)	108.6(7)
C(11)–C(12)–N(3)	110.6(6)
C(13)–C(12)–N(3)	112.4(6)
C(12)–C(13)–C(14)	115.7(7)
C(13)–C(14)–C(15)	123.4(9)
C(13)–C(14)–C(17)	128.7(9)
C(15)–C(14)–C(17)	107.9(8)
C(14)–C(15)–N(4)	108.1(9)
C(17)–C(16)–C(21)	119.7(10)
C(17)–C(16)–N(4)	107.1(9)
C(21)–C(16)–N(4)	133.2(10)
C(14)–C(17)–C(16)	105.4(8)
C(14)–C(17)–C(18)	137.1(9)
C(16)–C(17)–C(18)	117.6(9)
C(17)–C(18)–C(19)	121.3(9)
C(18)–C(19)–C(20)	122.1(11)
C(19)–C(20)–C(21)	118.4(11)
C(16)–C(21)–C(20)	120.7(10)
Cu–N(1)–C(1)	113.8(5)
Cu–N(1)–C(5)	127.9(5)
C(1)–N(1)–C(5)	117.8(7)
Cu–N(2)–C(6)	116.0(5)
Cu–N(2)–C(10)	126.4(6)
C(6)–N(2)–C(10)	117.5(7)
Cu–N(3)–C(12)	107.6(5)
C(15)–N(4)–C(16)	111.5(8)
Cu–O(1)–C(11)	113.4(5)

[a] e.s.d.s are given in parentheses. [b] The primed atoms are related to unprimed ones by the transformation $1-x$, $\frac{1}{2}+y$, $1-z$.

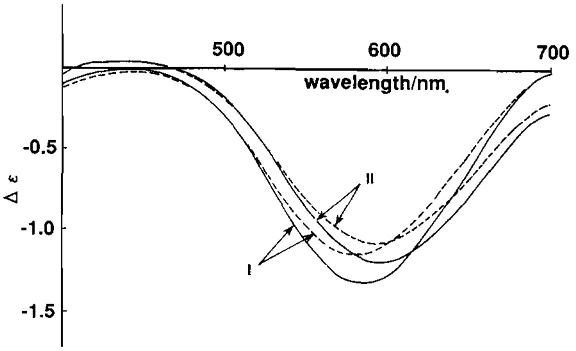

Fig. 3. Solvent dependences of CD spectra of [Cu(bpy)(L-trp)]ClO_4 (I) and [Cu(phen)(L-trp)]ClO_4 (II) in the d–d region. Solvents: water (——), 60 vol.% dioxane–40 vol.% water (-----).

Discussion

As is obvious from Fig. 2, the most interesting structural feature found in **I** is the extensive intramolecular stacking formation between the bpy ring and the indole ring of L-trp with the average spacing of 3.67 Å. The indole ring is stacked on the bpy ring with a tilting angle of 6° between the two planes. Significant deviation of the β-carbon, C(12), from the coordination plane formed by N(1), N(2), N(3) and O(1) toward the indole ring makes the parallel arrangement with the bpy ring feasible. Similar intramolecular stacking is also found in the previously reported complex [Cu(phen)(L-trp)]ClO_4 [19, 22]. Examination of these two structures (Fig. 5) reveals that the stacking mode in $[Cu(bpy)(L\text{-}trp)]^+$ corresponds well with that in $[Cu(phen)(L\text{-}trp)]^+$ except that the indole rings in both structures are stacked on DA with the plane reverse to each other. It seems that these interaction modes between the indole and the aromatic diamine ring and between the indole ring and the Cu(II) ion are the most stable ones. The intramolecular stacking interaction in **II** may be stronger as compared with that in **I**, since the average spacings are shorter for the former (3.51 Å) than for the latter (3.67 Å). The close contacts between the Cu(II) ion and the carbon atoms of the indole ring are clearly seen from the Cu...3-C(indole) distances, 3.35 and 3.20 Å, and the Cu...4a-C(indole) distances, 3.29 and 3.25 Å, in **I** and **II** [19], respectively. The subtle differences observed in these structures may be due to the difference between the affinities of phen and bpy for the indole ring, while such a short contact is understandable on the basis of the π-electron density which is highest on these two carbon atoms.

Stacking in solution

In aqueous solution an aromatic compound tends to form a hydrophobic interaction with the other aromatic compound. Addition of a less polar solvent such as dioxane into the solution reduces the hydrophobic interaction, and the aromatic rings dissociate from each other. Such a phenomenon was also observed for solutions of **I** and **II**. Their CD spectra in the d–d region in water show a large negative peak, which are greatly weakened in 60% aqueous dioxane. This implies an increase of the

TABLE 4. Absorption and CD spectral data in the d–d region for [Cu(bpy)(L-trp)]ClO$_4$ (I) and [Cu(phen)(L-trp)]ClO$_4$ (II)

Complex	Absorption		CD				$r(\Delta\epsilon)^b$
			In water		In dioxane–water^a		
	λ_{max} (nm)	ϵ (M(Cu)$^{-1}$ cm^{-1})	$\lambda_{\Delta\epsilon max}$ (nm)	$\Delta\epsilon_w$ (M(Cu)$^{-1}$ cm^{-1})	$\lambda_{\Delta\epsilon max}$ (nm)	$\Delta\epsilon_d$ (M(Cu)$^{-1}$ cm^{-1})	
[Cu(bpy)(L-trp)]ClO$_4$ (I)	600	67	587	−1.31	582	−1.15	0.91
[Cu(phen)(L-trp)]ClO$_4$ (II)	611	74	598	−1.22	596	−1.11	0.88

^{a}Measured in 60 vol.% dioxane–water. $^b r(\Delta\epsilon) = \Delta\epsilon_d/\Delta\epsilon_w$; $\Delta\epsilon_d$: magnitude in 60 vol.% dioxane; $\Delta\epsilon_w$: magnitude in water.

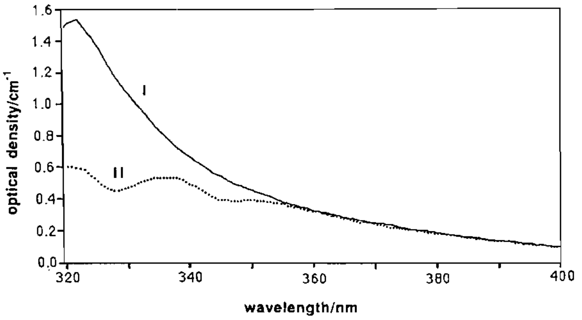

Fig. 4. Difference absorption spectra indicating charge transfer between the aromatic diamine and indole rings in water. Curves: I, {[Cu(bpy)(L-trp)]ClO$_4$} − {[Cu(bpy)(L-alanine)]ClO$_4$ + L-trp}; II, {[Cu(phen)(L-trp)]ClO$_4$} − {[Cu(phen)(L-alanine)]ClO$_4$ + L-trp}.

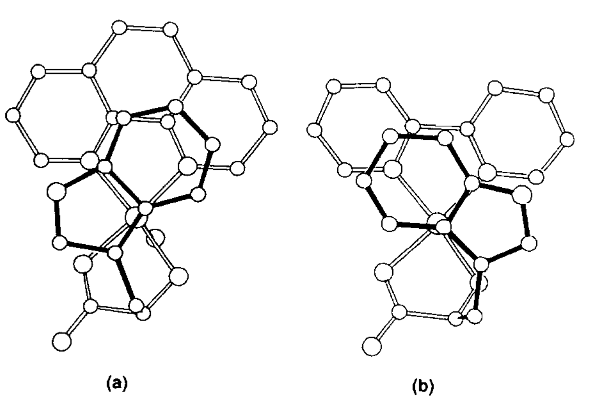

Fig. 5. Comparison of stacking modes in [Cu(phen)(L-trp)]ClO$_4$ (II) (a) and [Cu(bpy)(L-trp)]ClO$_4$ (I) (b).

torsion angle (Cu)O–C(O)–C$_\alpha$–C$_\beta$ and a weaker vicinal effect [31]. The ratio of the CD spectral magnitude in aqueous dioxane to that in water ($r(\Delta\epsilon)$) (Table 4) is 0.88 and 0.91 for **I** and **II**, respectively. The fact that the latter is slightly less susceptible to the addition of dioxane as compared with the former may indicate that the hydrophobic interaction between phen and indole in **II** is stronger than that between bpy and indole in **I**. This is consistent with the ring size of DA and the separation between the rings in the solid state.

Charge transfer due to stacking

The stacking interaction generally arises from the interaction between the π-orbitals of two aromatic rings, especially between the highest occupied molecular orbital (HOMO) of the donor ring and the lowest unoccupied molecular orbital (LUMO) of the acceptor ring. It often gives rise to CT absorption bands in the near UV region [32]. For the present ternary systems, the difference between the spectral magnitudes observed for the complexes and the sum of the spectral magnitudes for their components, [Cu(DA)(L-alanine)]ClO$_4$ and L-trp, gave a weak and broad band near 320 nm. This is assigned to the charge transfer between indole and DA, because a similar absorption was observed at 360 nm for the system [H(phen)(L-trpH$_2$)] not involving copper(II) [12], and analogous CT bands have also been reported for the systems with indoles and oxidized nicotinamide-adenine dinucleotide having a positive charge [33]. The CT absorption in the present cases is probably due to charge transfer from the electron-rich indole [6] to electron-deficient coordinated aromatic diamines.

Conclusions

The present study revealed that stacking occurs between the aromatic rings incorporating coordinated nitrogens and the side-chain indole ring of coordinated L-trp in aqueous solution and in the crystalline state. A close contact was also observed between the copper(II) ion and the indole ring. As shown in a previous study the stacking interaction contributes to the stability of the ternary complex [12], although the stabilization due to the Cu(II)–aromatic ring contact is small. The present study suggests the importance of the tryptophan residue in selective interactions with the other aromatic rings in biological systems.

References

1 R. Barker, in *Organic Chemistry of Biological Compounds*, Prentice-Hall, Englewood Cliffs, NY, 1971.
2 W. P. Jencks, *Adv. Enzymol., 43* (1975) 219.
3 E. Frieden, *J. Chem. Educ., 52* (1975) 754.
4 T. P. Singer (ed.), in *Flavin and Flavoproteins* (Proc. 5th Int. Symp.), Elsevier, Amsterdam, 1976.
5 C. A. Hunter and J. K. Sanders, *J. Am. Chem. Soc., 112* (1990) 5525.
6 B. Pullman and A. Pullman, *Proc. Natl. Acad. Sci. U.S.A., 44* (1958) 1197.
7 M. A. Slifkin, in *Charge Transfer Interactions of Biomolecules*, Academic Press, London, 1971.
8 H. Sigel, *Pure Appl. Chem., 61* (1989) 923.
9 A. Odani and O. Yamauchi, *Inorg. Chim. Acta, 93* (1984) 13.
10 O. Yamauchi and A. Odani, *Inorg. Chim. Acta, 100* (1985) 165.
11 O. Yamauchi, K. Tsujide and A. Odani, *J. Am. Chem. Soc., 107* (1985) 659.
12 O. Yamauchi and A. Odani, *J. Am. Chem. Soc., 107* (1985) 5938.
13 A. Odani, S. Deguchi and O. Yamauchi, *Inorg. Chem., 25* (1986) 62.
14 O. Yamauchi and A. Odani, *Nippon Kagaku Kaishi,* (1988) 369.
15 H. Sigel, R. Tribolet and O. Yamauchi, *Comments Inorg. Chem., 9* (1990) 305.
16 H. Sigel, *Angew. Chem., Int. Ed. Engl., 14* (1975) 394.
17 H. Sigel, B. E. Fischer and B. Prijs, *J. Am. Chem. Soc., 99* (1977) 4489.
18 D. Banerjea, T. A. Kaden and H. Sigel, *Inorg. Chem., 20* (1981) 2586.
19 H. Masuda, O. Matsumoto, A. Odani and O. Yamauchi, *Nippon Kagaku Kaishi,* (1988) 783.
20 H. Masuda, A. Odani and O. Yamauchi, *Inorg. Chem., 28* (1989) 624.
21 O. Yamauchi, A. Odani, T. Kohzuma, H. Masuda, K. Toriumi and K. Saito, *Inorg. Chem., 28* (1989) 4066.
22 K. Aoki and H. Yamazaki, *J. Chem. Soc., Dalton Trans.,* (1987) 2017.
23 J. A. Ibers and W. C. Hamilton (eds.), *International Tables for X-Ray Crystallography,* Vol. IV, Kynoch, Birmingham, U.K., 1974.
24 T. Taga, T. Iizuka, and T. Higashi, *KPPXRAY,* Kyoto program package for X-ray crystal structure analysis, Kyoto University, 1985.
25 W. C. Hamilton, *Acta Crystallogr., 12* (1959) 609.
26 D. van der Helm and C. E. Tatsch, *Acta Crystallogr., Sect. B, 28* (1972) 2307.
27 H. C. Freeman, *Adv. Protein Chem., 22* (1967) 257.
28 A. Pajunen and S. Pajunen, *Acta Crystallogr., Sect. B, 38* (1982) 3093.
29 A. F. Wells, *Structural Inorganic Chemistry,* Oxford University Press, New York, 1975, p. 259.
30 I. M. Procter, B. J. Hatherway and P. Nicholls, *J. Chem. Soc. A,* (1968) 1678.
31 T. Yasui, J. Hidaka and Y. Shimura, *J. Am. Chem. Soc., 87* (1965) 2762.
32 C. F. Nauman and H. Sigel, *J. Am. Chem. Soc., 96* (1974) 2750.
33 S. G. A. Alivisatos, F. Ungar, A. Jibril and G. A. Mourkides, *Biobchim. Biophys. Acta, 51* (1961) 361.