Bull. Chem. Soc. Jpn., 72, 981—988 (1999)

Structural Evidence for an Intramolecular CH–π Interaction in Ternary Metal (Cu(II), Pd(II)) Complexes Involving *o*-/*m*-/*p*-Methyl Substituted Phenylalanine and 1,10-Phenanthroline

Mamoru Mizutani, Shinya Tomosue, Hitoshi Kinoshita, Koichiro Jitsukawa,* Hideki Masuda,* and Hisahiko Einaga

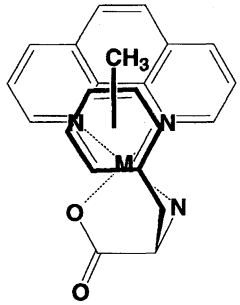
Department of Applied Chemistry, Nagoya Institute of Technology, Showa-ku, Nagoya 466-8555

(Received October 12, 1998)

The existence of a CH-π interaction has clearly been demonstrated by use of the ternary metal (Cu(II), Pd(II)) complexes involving *o*-/*m*-/*p*-methyl substituted L-phenylalanine (L-*o*-mPhe, L-*m*-mPhe, L-*p*-mPhe) and 1,10-phenanthroline (phen) on the basis of ^{1}H NMR, electronic absorption, and CD spectroscopies, and X-ray diffraction method. The crystal structure of $[\{Cu(p\text{-mPhe})(phen)\}_2\{Cu(phen)_2\}(\mu_3\text{-}CO_3)](ClO_4)_2$ has revealed a marked structural feature suggesting CH-π and/or π–π interactions, although $[Cu(L\text{-}o\text{-mPhe})(phen)(H_2O)]ClO_4$ does not show any interaction. CD spectra in the d–d region for $[Cu(L\text{-}o\text{-mPhe})(phen)]ClO_4$, $[Cu(L\text{-}m\text{-mPhe})(phen)]ClO_4$, and $[Cu(L\text{-}p\text{-mPhe})(phen)]ClO_4$ in aqueous solution have exhibited an obvious negative Cotton effect, and the magnitudes have significantly been reduced in dioxane/water in the order: $[Cu(L\text{-}p\text{-mPhe})(phen)]ClO_4 \leq [Cu(L\text{-}m\text{-mPhe})(phen)]ClO_4 < [Cu(L\text{-}o\text{-mPhe})(phen)]ClO_4$. ^{1}H NMR spectra of $[Pd(L\text{-}o\text{-mPhe})(phen)]ClO_4$, $[Pd(L\text{-}m\text{-mPhe})(phen)]ClO_4$, and $[Pd(L\text{-}p\text{-mPhe})(phen)]ClO_4$ have exhibited larger ring current shifts for *m*- and *p*-CH_3 protons of the latter two complexes both in D_2O and in DMSO-d_6, whereas *o*-CH_3 protons for the former complex do not. The magnitudes have greatly been reduced in this order: $[Pd(L\text{-}p\text{-mPhe})(phen)]ClO_4 \leq [Pd(L\text{-}m\text{-mPhe})(phen)]ClO_4$ in D_2O–dioxane-d_8, but not for $[Pd(L\text{-}o\text{-mPhe})(phen)]ClO_4$.

Weak non-covalent interactions, such as hydrogen bonding and hydrophobic and electrostatic interactions, contribute to the regulation in the formation of supramolecular structures[1] and in the rigorously arranged complexes in reaction intermediates.[2] In complexation of a protein with a substrate in the specific site of enzyme receptor, their interactions are a key step for demonstrating high-efficiency and -specificity in a biochemical reaction.[3] Recently, a CH-π interaction occurring between CHs (soft acids) and π-groups (soft bases) has also been noted as one more weak hydrogenbond-like force by many chemists and biochemists.[4—8] Many suggestions and some evidence for the presence of such an interaction[9,10] have been accumulated from experimental studies on conformational problems of a series of compounds bearing both an aliphatic group and a phenyl group on the molecule. Most of them are fortunately discovered, and we could find it through a study on the structural significance of pyridoxal 2-methyl group of pyridoxylideneamino acid in amino acid metabolism,[11—13] in which α-hydroxylation of amino acids was controlled by the simple Co(III) binary complex containing pyridoxylideneamino acid ligand through the CH-π interaction. However, it is very difficult to experimentally and directly prove such an interaction, because it is very weak in comparison with the other non-covalent interactions and can easily be disturbed by them.

In order to clarify the evidence of the CH-π interaction, we have newly designed ternary metal (Cu(II), Pd(II)) complexes with L-*o*-/*m*-/*p*-methylphenylalanine (L-*o*-/*m*-/*p*-mPhe) and 1,10-phenanthroline (phen) as the structural models, as shown in Scheme 1. In these complexes, [M(L-*o*-/*m*-/*p*-/mPhe)(phen)]X (M = Cu(II) or Pd(II); X^- = anion), the CPK model suggested the following possibility: Intramolecular CH-π interaction between phen and substituted methyl groups is possible in the case of the complexes with L-*m*-/*p*-mPhe, whereas it is impossible in the case of those with L-*o*-mPhe. Detailed examination of their ternary metal complexes by use of electronic absorption, circular dichroism (CD), and ^{1}H NMR spectroscopies and X-ray diffraction method has given direct structural evidence of the existence of the CH-π interaction.



Scheme 1. Possible CH-π and π–π interactions in $[M^{II}$-(L-*o*-/*m*-/*p*-mPhe)(phen)$]^+$.

Experimental

Materials. Reagents and solvents employed were of the highest grade available and furthermore were purified before use. L-*o*-, *m*-, and *p*-Methyl substituted phenylalanine derivatives (L-*o*-, *m*-, *p*-mPhe) were synthesized according to Strecker's method.[14] Optically active L-*o*-/*m*-/*p*-mPhe derivatives were prepared by a modification of Izumiya's method.[15]

Preparation of Binary and Ternary Palladium Complexes. Binary palladium complexes, [Pd(L-*o*-/*m*-/*p*-mPhe)$_2$], were prepared as follows. To a solution of $PdCl_2$ (50 mg, 0.28 mmol) in 1 M HCl (5 mL, 1 M = 1 mol dm^{-3}) was added a dilute HCl solution (5 mL) of mPhe (100 mg, 0.56 mmol), and then pH was adjusted to pH 6—7 with aqueous NaOH solution.

[Pd(L-*o*-mPhe)$_2$]: ^{1}H NMR (DMSO-d_6) δ = 2.26 (s, 3H, *o*-CH_3), 2.78 (dd, 1H, J = 10.8, 14.9 Hz, β-CH_2–), 3.08 (dd, 1H, J = 3.0, 14.9 Hz, β-CH_2–), 3.25—3.60 (m, 1H, α-CH<), 7.06—7.21 (m, 4H, *o*-/*m*-/*m*′-/*p*-H).

[Pd(L-*m*-mPhe)$_2$]: ^{1}H NMR (DMSO-d_6) δ = 2.24 (s, 3H, *m*-CH_3), 2.71 (dd, 1H, J = 11.3, 14.1 Hz, β-CH_2–), 2.97 (d, 1H, J = 14.1 Hz, β-CH_2–), 3.20—3.56 (m, 1H, α-CH<), 6.95—7.24 (m, 4H, *o*-/*o*′-/*m*′-/*p*-H).

[Pd(L-*p*-mPhe)$_2$]: ^{1}H NMR (DMSO-d_6) δ = 2.26 (s, 3H, *p*-CH_3), 2.72 (dd, 1H, J = 10.3, 14.4 Hz, β-CH_2–), 2.95 (dd, 1H, J = 3.6, 14.4 Hz, β-CH_2–), 3.20—3.50 (m, 1H, α-CH<), 7.05—7.20 (m, 4H, *o*-/*o*′-/*m*-/*m*′-H).

Ternary palladium complexes, [Pd(L-*o*-/*m*-/*p*-mPhe)(phen)]ClO_4 (phen = 1,10-phenanthroline), were prepared as follows. To a solution of $PdCl_2$ (50 mg, 0.28 mmol) in 1 M HCl (5 mL) was added a dilute HCl solution (5 mL) of mPhe (100 mg, 0.56 mmol), and then pH was adjusted to pH 6—7 with aqueous NaOH solution. The resulting binary palladium complex, [Pd(L-mPhe)$_2$], was treated with an equimolar amount of phen (55 mg, 0.30 mmol) in aqueous methanol solution (5 mL), which was stirred overnight at 40 °C. The addition of aqueous solution of $NaClO_4$ to the reaction mixture gave a precipitate of the ternary palladium complex.

[Pd(L-*o*-mPhe)(phen)]ClO_4 (1P): Yield 89%, pale-yellow crystals, ^{1}H NMR (DMSO-d_6) δ = 2.35 (s, 3H, *o*-CH_3), 3.01 (dd, 1H, J = 9.3, 15.1 Hz, β-CH_2–), 3.31 (dd, 1H, J = 4.0, 15.1 Hz, β-CH_2–), 3.87—4.03 (m, 1H, α-CH<), 7.05—7.20 (m, 3H, *m*-/*m*′-/*p*-H), 7.39 (d, 1H, J = 5.6 Hz, *o*′-H), 8.16 (dd, 2H, J = 5.4, 8.3 Hz, phen 3,8-H), 8.31 (s, 2H, phen 5,6-H), 8.81 (d, 2H, J = 5.4 Hz, phen 4,7-H), 9.02 (d, 2H, J = 8.3 Hz, phen 2,9-H).

[Pd(L-*m*-mPhe)(phen)]ClO_4 (2P): Yield 93%, pale-yellow crystals, ^{1}H NMR (DMSO-d_6) δ = 1.96 (s, 3H, *m*-CH_3), 3.04 (dd, 1H, J = 7.4, 14.7 Hz, β-CH_2–), 3.17 (dd, 1H, J = 4.0, 14.7 Hz, β-CH_2–), 3.94—4.04 (m, 1H, α-CH<), 6.74 (d, 1H, J = 7.4 Hz, *p*-H), 7.01 (t, 1H, J = 7.4 Hz, *m*-H), 7.16 (d, 1H, J = 7.4 Hz, *o*′-H), 7.21 (s, 1H, *o*-H), 8.12 (dd, 1H, J = 5.2, 8.2 Hz, phen 3,8-H), 8.17 (dd, 1H, J = 5.2, 8.2 Hz, phen 3,8-H), 8.29 (s, 2H, phen 5,6-H), 8.66 (d, 1H, J = 5.2 Hz, phen 4,7-H), 8.84 (d, 1H, J = 5.2 Hz, phen 4,7-H), 8.99 (d, 1H, J = 8.2 Hz, phen 2,9-H), 9.02 (d, 1H, J = 8.2 Hz, phen 2,9-H).

[Pd(L-*p*-mPhe)(phen)]ClO_4 (3P): Yield 98%, pale-yellow crystals, ^{1}H NMR (DMSO-d_6) δ = 1.89 (s, 3H, *p*-CH_3), 3.03 (dd, 1H, J = 7.4, 14.2 Hz, β-CH_2–), 3.15 (dd, 1H, J = 4.2, 14.2 Hz, β-CH_2–), 3.90—4.00 (m, 1H, α-CH<), 6.86 (d, 2H, J = 7.8 Hz, *m*-H), 7.25 (d, 2H, J = 7.8 Hz, *o*-H), 8.13 (dd, 1H, J = 5.2, 8.2 Hz, phen 3,8-H), 8.16 (dd, 1H, J = 5.2, 8.2 Hz, phen 3,8-H), 8.30 (s, 2H, phen 5,6-H), 8.67 (d, 1H, J = 5.2 Hz, phen 4,7-H), 8.82 (d, 1H, J = 5.2 Hz, phen 4,7-H), 9.01 (d, 1H, J = 8.2 Hz, phen 2,9-H), 9.03 (d, 1H, J = 8.2 Hz, phen 2,9-H).

Preparation of Ternary Copper Complexes. Ternary copper(II) complexes, [Cu(L-mPhe)(phen)]ClO_4, were prepared as follows. To an equimolar amount of $Cu(ClO_4)_2 \cdot 6H_2O$ (220 mg, 0.6 mmol) and phen (110 mg, 0.6 mmol) in aqueous methanol solution (5 mL, 50 v/v%) was added mPhe (110 mg, 0.6 mmol) in 1 M NaOH (5 mL) at room temperature. The mixture was stirred to complete dissolution; the crystals which separated on standing at room temperature were collected and recrystallized from aqueous methanol to give the following analytically pure complexes.

[Cu(L-*o*-mPhe)(phen)]$ClO_4 \cdot H_2O$ (1C): Yield 86%, blue crystals, Anal. Calcd for $C_{22}H_{20}N_3O_6CuCl \cdot H_2O$: C, 48.99; H, 4.11; N, 7.79%. Found: C, 48.63; H, 4.01; N, 7.72%.

[Cu(L-*m*-mPhe)(phen)]$ClO_4 \cdot 1.5H_2O$ (2C): Yield 84%, blue crystals, Anal. Calcd for $C_{22}H_{20}N_3O_6CuCl \cdot 1.5H_2O$: C, 48.18; H, 4.23; N, 7.66%. Found: C, 48.10; H, 3.82; N, 7.68%.

[Cu(L-*p*-mPhe)(phen)]$ClO_4 \cdot 1.5H_2O$ (3C): Yield 90%, blue crystals, Anal. Calcd for $C_{22}H_{20}N_3O_6CuCl \cdot 1.5H_2O$: C, 48.18; H, 4.23; N, 7.66%. Found: C, 47.99; H, 3.79; N, 7.61%.

Spectral Measurements. Absorption spectra were measured on a JASCO UVIDEC-660 spectrophotometer and circular dichroism (CD) spectra were obtained with a JASCO J-600 spectropolarimeter, in quartz cells with an optical path length of 1.0 cm for 10 mM solution at room temperature. ^{1}H NMR spectra were recorded on a JEOL Lambda 500 MHz or a Varian Gemini XL-200 spectrometer in DMSO-d_6, D_2O, and D_2O–dioxane-d_8 with TMS or DSS, respectively, as an internal standard. Samples for all measurements were freshly prepared before use, the concentrations being adjusted at 1 or 10 mM with respect to Pd(II).

X-Ray Crystal Structure Determinations of the [Cu(L-*o*-mPhe)(phen)]ClO_4 (1C) and [{Cu(*p*-mPhe)(phen)}$_2${Cu(phen)$_2$}(μ_3-CO_3)]$(ClO_4)_2$ (3C′). Prismatic single crystals of **1C** suitable for X-ray analysis were obtained from the aqueous methanol solution by slow evaporation at room temperature. The plate-like single crystals containing **3C** were accidentally obtained as [{Cu(*p*-mPhe)(phen)}$_2${Cu(phen)$_2$}(μ_3-CO_3)]$(ClO_4)_2$ (**3C′**) from an aqueous methanol solution, followed by standing for one month, although that of the optically active complex was not generated. Single crystals of **1C** and **3C′** were mounted on a glass capillary. Diffraction data were collected with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å) on an Enraf Nonius CAD4-EXPRESS four-circle diffractometer. The crystal data and details of the parameters associated with data collection for the crystals **1C** and **3C′** are given in Table 1. The unit cell parameters were derived from least-squares refinement of 25 well-centered reflections. The reflection intensities were monitored by three standard reflections every 2 h, and the decay of intensities was within 2%. Reflection data were corrected for the Lorentz and polarization effects. Empirical absorption corrections, based on Ψ scans, were applied.

The structures of the complexes were solved by the heavy-atom method and refined by anisotropically least-squares calculations. Refinements were continued until all shifts were smaller than one-third of the standard deviations of the parameters involved. The carbonate anion in **3C′** was assigned from the bond parameters and the electron density analysis. Atomic scattering factors and anomalous dispersion terms were taken from the literature.[16] A part of the hydrogen atoms were located from the difference Fourier maps and the others were constrained to ideal geometries with C–H = 0.95 Å, and their parameters were isotropically refined. The R and R_w values were 0.056 and 0.060 for **1C** and 0.096 and 0.086 for **3C′**, respectively. The weighting scheme $w^{-1} = \sigma^2(F_o)$ was employed for both crystals. The final difference Fourier maps did not show any significant features for all crystals. The calculations

Table 1. Crystal Data and Experimental Details for **1C** and **3C′**

Complex	**1C**	**3C′**
Formula	$Cu(C_{22}H_{20}N_3O_2)ClO_4 \cdot H_2O$	$Cu_3(C_{68}H_{56}N_{10}O_4) \cdot CO_3 \cdot (ClO_4)_2 \cdot 5H_2O$
Formula weight	539.43	1616.88
Color	Blue	Blue
Crystal size/mm	$0.20 \times 0.20 \times 0.20$	$0.10 \times 0.30 \times 0.40$
Crystal system	Monoclinic P	Monoclinic P
Space group	$P2_1$ (#4)	$P2/c$ (#13)
a/Å	6.0262(3)	18.165(2)
b/Å	19.9570(8)	12.594(1)
c/Å	9.7746(3)	30.257(6)
β/°	93.392(4)	99.75(1)
V/Å^3	1173.48(7)	6821(1)
Z	2	4
Scan mode	ω–2θ	ω–2θ
$2\theta_{max}$/deg	52.64	48.5
D_{calcd}/g cm^{-3}	1.527	1.574
μ(Mo $K\alpha$)/cm^{-1}	10.93	10.89
T/K	293	293
F (000)	554.00	3324.00
No. of refls. obsd	5230	12008
No. of refls. used ($\|I_o\| > 3\sigma\|I_o\|$)	2225	3180
R	0.056	0.096
R_w	0.060	0.086

were performed on an IRIS Indigo XS-24 workstation using the program system teXsan.[17] Tables of atomic coordinates, anisotropic temperature factors, bond lengths and angles, and observed and calculated structure factors were deposited as Document No. 72015 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Absorption and CD Spectral Properties of Ternary Copper(II) Complexes with L-*o*-/*m*-/*p*-mPhe and phen. The ternary complexes [Cu(L-*o*-/*m*-/*p*-mPhe)(phen)]ClO_4 (**1C**, **2C**, **3C**) in an aqueous solution showed a broad d–d absorption peak near 610—620 nm with a tailing in the longer wavelength side at neutral pH (Table 2). All the three spectra exhibited the same spectral patterns that are characteristic of a square pyramidal copper coordination,[18] indicating that the coordination environments around the copper(II) ions of all the complexes are similar. All these complexes in an aqueous solution also exhibited a negative CD maximum near 590 nm at neutral pH due to the d–d splitting (Table 2). For the ternary complexes of amino acids, the CD magnitudes have been known to be an additive function of the magnitudes of the component complexes in the absence of the ligand–ligand interactions, but this magnitude deviates from the additivity when through-space or through-bond ligand–metal–ligand interactions exist.[19—21] The deviation from additivity is interpreted as being due to increased asymmetry arising from limited side chain motion. The magnitudes of the negative peak of [Cu(L-*o*-/*m*-/*p*-mPhe)(phen)]ClO_4 in water, $\Delta\varepsilon$ (H_2O), are reduced in less polar solvents, such as 36 and 54 (v/v)% dioxane–water (D_{36}, D_{54}). The extent of the CD magnitude decrease at the maximum wavelength, $\Delta\varepsilon_{36}$ or $\Delta\varepsilon_{54}$ defined as $[\Delta\varepsilon(H_2O) - \Delta\varepsilon(D_{36}$ or $D_{54})] \cdot 100/\Delta\varepsilon(H_2O)$, is in the order of [Cu(L-*p*-mPhe)(phen)]$ClO_4 \leq$ [Cu(L-*m*-mPhe)-(phen)]$ClO_4 <$ [Cu(L-*o*-mPhe)(phen)]ClO_4, indicating that the decrease reflect the existence of some intramolecular interaction, such as that between the methyl group and phen ring, which is weakened in hydrophobic environments. The consideration by the CPK model supports the above experimental results, because the methyl groups in [Cu(L-*m*-mPhe)-(phen)]ClO_4 and [Cu(L-*p*-mPhe)(phen)]ClO_4 complexes are able to interact intramolecularly with a phen ring, whereas such an interaction is not expected in [Cu(L-*o*-mPhe)(phen)]-

Table 2. Absorption and CD Spectral Data of Cu(II) Complexes

Compound	Absorption	CD			
	λ_{max}/ nm		$\Delta\varepsilon$/M(Cu)$^{-1}$ cm^{-1}		
	ε/M(Cu)$^{-1}$ cm^{-1}	$\Delta\varepsilon_{max}$/nm	H_2O	Dioxane 36%	Dioxane 54%
[Cu(L-*o*-mPhe)(phen)]ClO_4	616 (61)	600	−1.054	−0.906 (14.0)	−0.758 (28.1)
[Cu(L-*m*-mPhe)(phen)]ClO_4	615 (64)	585	−0.954	−0.837 (12.3)	−0.783 (17.9)
[Cu(L-*p*-mPhe)(phen)]ClO_4	620 (62)	585	−0.760	−0.730 (4.0)	−0.667 (12.2)

ClO_4 complex.

Crystal Structures of the [Cu(L-*o*-mPhe)(phen)]ClO_4 (1C) and [{Cu(*p*-mPhe)(phen)}$_2${Cu(phen)$_2$}(μ_3-CO_3)]-(ClO_4)$_2$ (3C′) Complexes. Single crystals of **1C** and **3C′** suitable for X-ray analysis were fortunately obtained, although they are slightly small. Their selected bond lengths and angles are given in Table 3. Their crystal structures (Figs. 1 and 2) exhibited very interesting structural differences, as described below.

Figure 1 shows a perspective view of complex **1C**, where the central Cu(II) ion is coordinated phen and L-*o*-mPhe (Cu(1)-N(1P) = 2.018(5), Cu(1)–N(12P) = 1.985(5), Cu(1)–O(91) = 1.925(4), Cu(1)–N(8) = 2.025(6) Å) in the square plane and one water molecule at an apical position (Cu(1)–O(1W) = 2.26(1) Å) to form a square pyramid. The bond lengths around the Cu atom agree well with those reported for five-coordinate Cu(II) complexes.[22—24] The side chain aromatic ring of L-*o*-mPhe is located approximately perpendicular to the coordination plane and showed an "open" form without any intramolecular π–π and

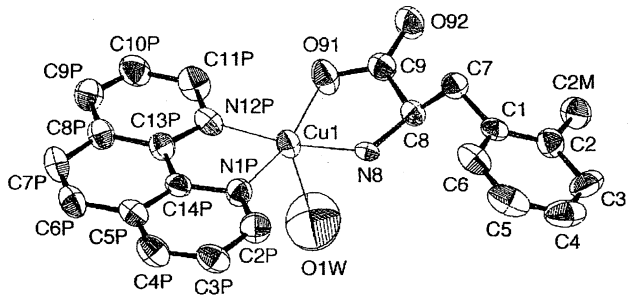


Fig. 1. Structure of [Cu(L-*o*-mPhe)(phen)(H_2O)]$^+$ (**1C**). The perchlorate anion was omitted for clarity.

XH-π interactions, which is very similar to the conformations which appear in the crystal structures reported previously: [Cu(L-Phe)(bpy)(H_2O)]ClO_4·H_2O,[24] [Cu(L-Phe)-(phen)Cl]·3H_2O,[24] and [Cu(L-Phe)(phen)]ClO_4·H_2O.[24]

The crystal of complex **3C′** contains two [Cu(*p*-mPhe)(phen)]$^+$, one [Cu(phen)$_2$]$^{2+}$, one CO_3^{2-}, and two ClO_4^- in the unit cell, in which the two [Cu(*p*-mPhe)-(phen)]$^+$ and [Cu(phen)$_2$]$^{2+}$ complexes are joined together by a CO_3^{2-} anion through the coordinate bonds between copper atoms and carbonato oxygens, as shown in Fig. 2a. The two independent [Cu(*p*-mPhe)(phen)]$^+$ complexes have essentially the same structure. Figures 2b and 2c show perspective and upright views, respectively, where each Cu(II) ion is coordinated phen and *p*-mPhe (Cu(1)–N(1PA) = 2.03(2), Cu(1)–N(12PA) = 1.97(2), Cu(1)–O(91A) = 1.94(2), Cu(1)–N(8A) = 2.01(2), Cu(2)–N(1PB) = 2.05(2), Cu(2)–N(12PB) = 2.00(2), Cu-(2)–O(91B) = 1.92(2), Cu(2)–N(8B) = 2.01(2) Å) in the square plane and carbonato oxygen at an apical position (Cu(1)–O(1CO) = 2.18(1), Cu(2)–O(2CO) = 2.19(1) Å) to form a square pyramid. The bond lengths around the Cu atom agree well with those reported for five-coordinate Cu-(II) complexes.[22—24] The structures exhibit a "closed" form with the intramolecular stacking between coordinating phen and aromatic ring of *p*-mPhe. The side chain aromatic ring of the amino acid in both structures is located approximately parallel to the coordination plane with the intramolecular stacking, with the average spacing of 3.51 and 3.62 Å for **3C′(A)** and **3C′(B)**, respectively. Significant deviation of the α-carbon (C(8B)) of amino acid from the coordination plane formed toward the phenyl ring makes the parallel arrangement with the phen ring feasible. The distances are comparable with those for [Cu(L-Trp)(bpy)]$^+$

Table 3. Intramolecular Distances and Bond Angles for **1C** and **3C′** [a]

[Cu(L-*o*-mPhe)(phen)(H_2O)]ClO_4 (**1C**)							
Cu(1)	N(8)		2.024(6)	Cu(1)	N(1P)		2.017(5)
Cu(1)	N(12P)		1.982(5)	Cu(1)	O(91)		1.925(4)
Cu(1)	O(1W)		2.26(1)				
N(8)	Cu(1)	N(1P)	96.7(2)	N(8)	Cu(1)	N(12P)	167.2(2)
N(1P)	Cu(1)	N(12P)	82.5(2)	N(8)	Cu(1)	O(91)	84.8(2)
N(8)	Cu(1)	O(1W)	90.3(4)	N(1P)	Cu(1)	O(91)	160.3(2)
N(12P)	Cu(1)	O(91)	91.7(2)	N(1P)	Cu(1)	O(1W)	94.2(4)
N(12P)	Cu(1)	O(1W)	102.5(4)	O(91)	Cu(1)	O(1W)	105.5(4)
[{Cu(*p*-mPhe)(phen)}$_2${Cu(phen)$_2$}(μ_3-CO_3)](ClO_4)$_2$·5H_2O (**3C′**)							
Cu(1)	N(8A)		2.00(2)	Cu(1)	N(1PA)		2.02(2)
Cu(1)	N(12PA)		1.94(2)	Cu(1)	O(91A)		1.94(2)
Cu(2)	N(8B)		2.01(2)	Cu(2)	N(1PB)		2.04(3)
Cu(2)	N(12PB)		2.01(2)	Cu(2)	O(91B)		1.92(2)
N(8A)	Cu(1)	N(1PA)	101(1)	N(8A)	Cu(1)	N(12PA)	146.2(8)
N(8A)	Cu(1)	O(91A)	82.6(9)	N(1PA)	Cu(1)	N(12PA)	79(1)
N(1PA)	Cu(1)	O(91A)	169.8(9)	N(12PA)	Cu(1)	O(91A)	92(1)
N(8B)	Cu(2)	N(1PB)	100(1)	N(8B)	Cu(2)	N(12PB)	153.7(8)
N(8B)	Cu(2)	O(91B)	84.6(9)	N(1PB)	Cu(2)	N(12PB)	80(1)
N(1PB)	Cu(2)	O(91B)	168(1)	N(12PB)	Cu(2)	O(91B)	90.6(9)

a) e.s.d.s are given in parentheses.

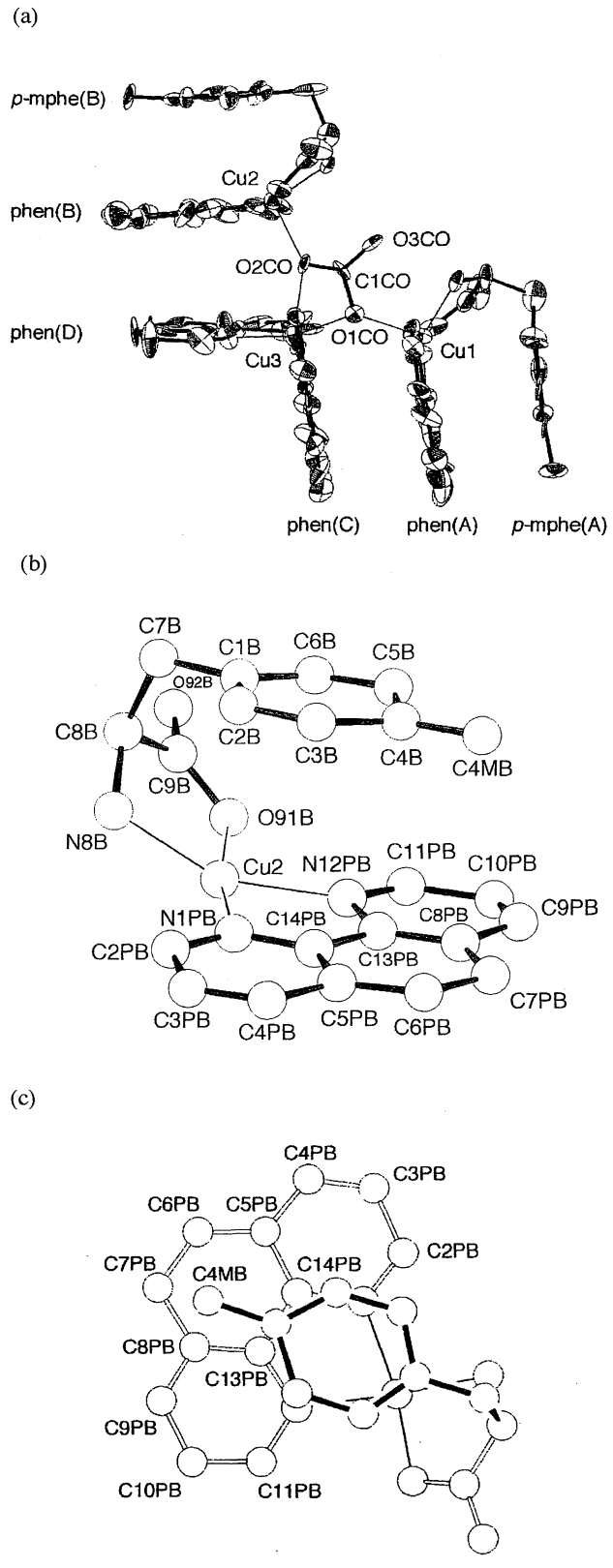


Fig. 2. (a) Structure of $[\{Cu(p\text{-}mPhe)(phen)\}_2\{Cu(phen)_2\}(\mu_3\text{-}CO_3)]^{2+}$ (**3C′**). The two perchlorate anions were omitted for clarity. (b) Perspective view of one of two crystallographically-independent molecules of $[Cu(p\text{-}mPhe)(phen)]^+$ (**B**). (c) Up-right view showing the CH–π interaction in $[Cu(p\text{-}mPhe)(phen)]^+$.

(Trp = tryptophanate; bpy = 2,2′-bipyridine),[23c] [Cu(L-Trp)(phen)]$^+$,[23a,23b] [Cu(L-Tyr)(bpy)]$^+$ (Tyr = tyrosinate),[19] and [Cu(L-Tyr)(phen)]$^+$ [24] with the distances of 3.67, 3.51, 3.35, and 3.33 Å, respectively. Interestingly, the *p*-methyl groups, as shown in Fig. 2c, are located just over the phen ring, with the closest methyl carbon–aromatic carbon atom distances of 3.54—4.01 Å, (3.54, 3.59, 3.76, and 3.93 Å for C(4MA)–C(7PA), C(4MA)–C(8PA), C(4MA)–C(9PA), and C(4MA)–C(13PA) and 3.86, 3.72, 3.97, and 4.01 Å for C(4MB)–C(7PB), C(4MB)–C(8PB), C(4MB)–C(9PB), and C(4MB)–C(13PB), respectively), which correspond well with an attractive approach between the iodine and bpy ring in [Cu(L-3-iodotyrosinato)(bpy)]$^+$ (3.59—3.72 Å).[25] and are relatively shorter also compared with the sum of the van der Waals radii of methyl group (2.0 Å) and aromatic carbon (1.7 Å).[26]

^{1}H NMR Spectra of Ternary Palladium Complexes with L-*o*-/*m*-/*p*-mPhe and phen. Since NMR spectroscopy is a powerful method for studying the weak interactions in solution,[27,28] ^{1}H NMR spectral behaviors of the corresponding Pd(II) complexes were examined in order to obtain more detailed structural information of the CH–π interaction in solutions. That dynamic structural features of the Cu(II) complexes obtained in solution can be mimicked by the corresponding Pd(II) complexes had already been reported by Yamauchi et al.,[21c,29] and we have approached them in the same sense. The existence of the CH–π and/or π–π interactions described above will be detected through the magnitude of the up-field-shifts of the protons in the vicinity of the rings due to the ring current effect.[30] Tables 4-1, 4-2, 4-3, and 5 give the ^{1}H NMR spectral data of the phenyl parts for the ternary Pd(II) complexes with L-*o*-/*m*-/*p*-mPhe and phen in D_2O, DMSO-d_6, and D_2O–dioxane-d_8 mixed solutions, together with those of metal free L-mPhe ligands and their binary Pd(II) complexes. The ^{1}H NMR chemical shifts of [Pd(L-*o*-/*m*-/*p*-mPhe)$_2$] complexes did not show any significant deviations in comparison with those of metal-free L-*o*-/*m*-/*p*-mPhe ligands, although there appeared little shifts due to complexation with metal ion. This finding suggests that few if any inter- and intramolecular interactions exist in the binary Pd(II) complexes in the concentration conditions measured. On the other hand, those of [Pd(L-*o*-/*m*-/*p*-mPhe)(phen)]ClO_4 complexes, **1P**, **2P**, and **3P**, exhibited very interesting spectral behaviors. All the *m*- and *p*-protons attached to the phenyl rings of **2P** and **3P** complexes, as shown in Tables 4-1, 4-2, 4-3, demonstrated up-field shifts both in D_2O and in DMSO-d_6, and the *o*-protons slightly shifted toward down-field, although those of complex **1P** did not show such a shift. These facts indicate that the *m*- and *p*-positions are shielded by the ring current effect to shift toward higher field but that the *o*-positions lie in the out-of-plane region beside the aromatic ring to shift toward lower field. Especially, the *m*- and *p*-methyl protons in the complexes **2P** and **3P**, respectively, gave rise to larger up-field shifts, in which the order of the up-field shifts from those of metal-free ligands is **1P** ≪ **2P** < **3P** both in D_2O and in DMSO-d_6. These up-field shifts are enhanced in more polar solvents such as D_2O than in DMSO-d_6, indicating that these

Table 4-1. ^{1}H NMR Spectra of L-*o*-Methylphenylalanine and Pd(II) Complexes[a)]

Compound	DMSO-d_6				D_2O				
	o'-	*m*-	*m'*-, *p*-	CH_3	*o'*-	*m*-	*m'*-	*p*-	CH_3
L-*o*-mPhe	7.21(d)	7.09(d)	7.13(t)	2.29(s)	7.28(d)		7.23–7.25(m)		2.36(s)
[Pd(L-*o*-mPhe)$_2$]	7.21(d)	7.04(d)	7.14–7.16(m)	2.26(s)	—	—	—	—	2.23(s)
[Pd(L-*o*-mPhe)(phen)]ClO_4	7.39(d)	7.09(d)	7.14(t)	2.35(s)	7.28(d)	6.86(d)	6.61(t)	6.71(t)	2.29(s)

a) ppm from DSS in D_2O. ppm from TMS in DMSO-d_6.

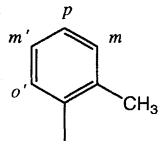


Table 4-2. ^{1}H NMR Spectra of L-*m*-Methylphenylalanine and Pd(II) Complexes[a)]

Compound	DMSO-d_6					D_2O				
	o-	*o'*-	*m'*-	*p*-	CH_3	*o*-	*o'*-	*m'*-	*p*-	CH_3
L-*m*-mPhe	7.07(s)	7.04(d)	7.17(t)	7.03(d)	2.27(s)	7.22(s)	7.14(d)	7.31(t)	7.11(d)	2.33(s)
[Pd(L-*m*-mPhe)$_2$]	7.00—7.03(m)		7.17(t)	7.00—7.03(m)	2.24(s)	7.01—7.05(m)		7.16(t)	7.01—7.05(m)	2.23(s)
[Pd(L-*m*-mPhe)(phen)]ClO_4	7.21(s)	7.16(d)	7.01(t)	6.74(d)	1.96(s)	7.20(s)	7.11(d)	6.66(t)	6.18(d)	1.37(s)

a) ppm from DSS in D_2O. ppm from TMS in DMSO-d_6.

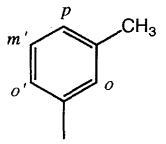
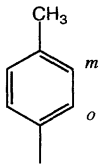


Table 4-3. ^{1}H NMR Spectra of L-*p*-Methylphenylalanine and Pd(II) Complexes[a)]

Compound	DMSO-d_6			D_2O		
	o-	*m*-	CH_3	*o*-	*m*-	CH_3
L-*p*-mPhe	7.12(d)		2.27(s)	7.22(d)		2.32(s)
[Pd(L-*p*-mPhe)$_2$]	7.11(d)		2.26(s)	7.13(d)		2.22(s)
[Pd(L-*p*-mPhe)(phen)]ClO_4	7.25(d)	6.86(d)	1.89(s)	7.19(d)	6.42(d)	1.14(s)

a) ppm from DSS in D_2O. ppm from TMS in DMSO-d_6.



shifts are governed by hydrophobic interactions. However, the findings that the *m*-Hs, *p*-Hs, *m*-CH_3, and *p*-CH_3 of **2P** and **3P** exhibited up-field shifts and that those of **1P** did not shift strongly suggest the existence of attractive CH-π interactions between the methyl group and phen ring. The strength is in the order of **1P** ≪ **2P** < **3P**, which agrees well with the result obtained from the CD spectral behaviors in the corresponding Cu(II) complexes. Such a CH-π interaction was also observed from the solvent effect of the ^{1}H NMR chemical shifts of these methyl protons (Table 5). The up-

Table 5. Change in the ^{1}H NMR Chemical Shift of Pd(II) Complexes with Addition of Dioxane[a,b)]

Compound	D_2O	Dioxane-d_8		
		20%	40%	60%
[Pd(L-*o*-mPhe)(phen)]ClO_4	2.29	2.35(0.06)	2.37(0.08)	2.39(0.10)
[Pd(L-*m*-mPhe)(phen)]ClO_4	1.37	1.52(0.15)	1.64(0.27)	1.77(0.40)
[Pd(L-*p*-mPhe)(phen)]ClO_4	1.14	1.31(0.17)	1.45(0.31)	1.61(0.47)

a) ppm from DSS. b) the parentheses denotes the magnutude of down-field shift from in D_2O.

field shifts observed in D_2O were cancelled out by addition of a less-polar solvent such as dioxane-d_8. The extent of the reduced shift of the methyl proton peak elucidates the existence of CH-π interaction. These results indicate that the methyl group of **1P** is not shielded by ring current effect but that those of **2P** and **3P** are affected; such results correspond well to those of CD spectra. These findings are also strongly supported from consideration of the CPK model. The *m*- and *p*-methyl groups in **2P** and **3P**, respectively, can intramolecularly interact with the phen ring, whereas the *o*-methyl group in **1P** finds it difficult to do so.

Conclusion

In order to clarify the existence of a CH-π interaction, we have newly designed and synthesized the ternary metal (Cu(II), Pd(II)) complexes with L-*o*-/*m*-/*p*-mPhe and phen, we have characterized the complexes in both solid and solution states by use of electronic absorption, CD, and ^{1}H NMR spectroscopies and by the X-ray diffraction method. In solid state, the ternary Cu(II) complex with L-*p*-mPhe reveals the CH-π and/or π–π interactions between *p*-methylphenyl group and phen ring, whereas that with L-*o*-mPhe does not show such an interaction. In solution state, both the CD spectra of **1C**, **2C**, and **3C** and the ^{1}H NMR spectra of **1P**, **2P**, and **3P** strongly support the existence of the attractive CH-π interaction. A lot of papers on the CH-π interactions have been reported hitherto, and many of them are accidentally-occurring cases. The findings described here give some direct evidence of the existence of the CH-π interaction, which is very important when we consider its contribution in nature and in the architectural design of supramolecules.

We thank Professor Osamu Yamauchi of Nagoya University for useful discussions. Thanks are due to the Research Center for Molecular Materials, the Institute for Molecular Science, for assistance in using the NMR (500 MHz) spectrometer. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, to which our thanks are due. H. M. gratefully acknowledges financial support by a grant from the Sumitomo Foundation.

References

1) a) L. Ouahab, *Chem. Mater.*, **9**, 1909 (1997); b) D. H. Cao, K. Chen, J. Fan, J. Manna, B. Olenyuk, J. A. Whiteford, and P. J. Stang, *Pure Appl. Chem.*, **69**, 1979 (1997); c) M. C. Fyfe and J. F. Stoddart, *Acc. Chem. Res.*, **30**, 393 (1997); d) D. Philip and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, **35**, 1154 (1996); e) I. A. Atkins, A. M. Groth, L. F. Lindoy, O. A. Matthews, and G. V. Meehan, *Pure Appl. Chem.*, **68**, 1231 (1996); f) P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, **30**, 502 (1997); g) B. Linton and A. D. Hamilton, *Chem. Rev.*, **97**, 1669 (1997). h) C. Piguet, G. Bernardinelli, and G. Hopfgartner, *Chem. Rev.*, **97**, 2005 (1997).

2) S. Gellman, *Chem. Rev.*, **97**, 1231 (1997).

3) R. E. Babine and S. L. Bender, *Chem. Rev.*, **97**, 1359 (1997).

4) M. Nishio and M. Hirota, *Tetrahedron*, **45**, 7201 (1989).

5) a) K. Kobayashi, Y. Asakawa, Y. Kikuchi, T. Toi, and Y. Aoyama, *J. Am. Chem. Soc.*, **115**, 2648 (1993); b) Y. Kikuchi and Y. Aoyama, *Bull. Chem. Soc. Jpn.*, **69**, 217 (1996).

6) H. Okawa, *Coord. Chem. Rev.*, **92**, 1 (1988).

7) M. Nishio, Y. Umezawa, M. Hirota, and Y. Takeuchi, *Tetrahedron*, **51**, 8665 (1995).

8) a) M. Karatsu, H. Suezawa, K. Abe, M. Hirota, and M. Nishio, *Bull. Chem. Soc. Jpn.*, **59**, 3529 (1986); b) H. Imai, S. Nakagawa, and E. Kyuno, *J. Am. Chem. Soc.*, **114**, 6719 (1992); c) H. Suezawa, A. Mori, M. Sato, R. Ehama, I. Arai, K. Sakakibara, M. Hirota, M. Nishio, and Y. Kodama, *J. Phys. Org. Chem.*, **6**, 399 (1993).

9) Y. Umezawa, S. Tsuboyama, K. Honda, J. Uzawa, and M. Nishio, *Bull. Chem. Soc. Jpn.*, **71**, 1207 (1998).

10) M. Nishio, M. Hirota, and Y. Umezawa, "The CH/π Interaction. Evidence, Nature, and Consequences," John Wiley & Sons, Inc., New York (1998).

11) K. Jitsukawa, T. Morioka, H. Masuda, H. Ogoshi, and H. Einaga, *Inorg. Chim. Acta*, **216**, 249 (1994).

12) a) K. Jitsukawa, K. Iwai, H. Masuda, H. Ogoshi, and H. Einaga, *Chem. Lett.*, **1994**, 303; b) K. Jitsukawa, K. Iwai, H. Masuda, H. Ogoshi, and H. Einaga, *J. Chem. Soc., Dalton Trans.*, **1997**, 3691.

13) a) K. Jitsukawa, T. Yamamoto, H. Masuda, and H. Einaga, *Chem. Lett.*, **1993**, 1693; b) K. Jitsukawa, T. Yamamoto, H. Takahashi, H. Masuda, and H. Einaga, *Chem. Lett.*, **1995**, 777.

14) D. T. Mowry, *Chem. Rev.*, **42**, 236 (1948).

15) N. Izumiya, S. Lee, T. Kanmera, and H. Aoyagi, *J. Am. Chem. Soc.*, **99**, 8346 (1977).

16) "International Tables for X-Ray Crystallography," ed by J. A. Ibers and W. C. Hamilton, Kynoch, Birmingham, U.K. (1974), Vol. IV.

17) "teXsan Crystal Structure Analysis Package," Molecular Structure Corporation (1985 and 1992).

18) B. J. Hatherway, in "Comprehensive Coordination Chemistry," ed by G. Willkinson, Pergamon, Oxford (1987), Vol. 4, pp. 533—774.

19) O. Yamauchi, A. Odani, and H. Masuda, *Inorg. Chim. Acta*, **198-200**, 749 (1990).

20) a) J. M. Tsangaris and R. B. Martin, *J. Am. Chem. Soc.*, **92**, 4255 (1970); b) R. B. Martin, *Met. Ions Biol. Syst.*, **1**, 129 (1974).

21) a) O. Yamauchi, *J. Mol. Catal.*, **23**, 255 (1984); b) O. Yamauchi, Y. Nakao, and A. Nakahara, *Bull. Chem. Soc. Jpn.*, **48**, 2572 (1975); c) O. Yamauchi and A. Odani, *J. Am. Chem. Soc.*, **103**, 391 (1981); d) O. Yamauchi and A. Odani, *Inorg. Chim. Acta*, **100**, 165 (1985).

22) A. G. Orpen, L. Brammer, F. K. Allen, O. Kennard, D. G. Watson, and R. Taylor, in "Strcucture Correlation," ed by H. -B. Burgi and J. D. Dunitz, VCH, New York (1994), Vol. 2.

23) a) K. Aoki and H. Yamazaki, *J. Chem. Soc., Dalton Trans.*, **1987**, 2017; b) H. Masuda, O. Matsumoto, A. Odani, and O. Yamauchi, *Nippon Kagaku Kaishi*, **1988**, 783; c) H. Masuda, T. Sugimori, A. Odani, and O. Yamauchi, *Inorg. Chim. Acta*, **180**, 73 (1991); d) T. Sugimori, K. Shibakawa, H. Masuda, A. Odani, and O. Yamauchi, *Inorg. Chem.*, **32**, 4951 (1993); e) T. Sugimori, H. Masuda, and O. Yamauchi, *Bull. Chem. Soc. Jpn.*, **67**, 131 (1994).

24) T. Sugimori, H. Masuda, N. Ohata, K. Koiwai, A. Odani, and O. Yamauchi, *Inorg. Chem.*, **36**, 576 (1997).

25) F. Zhang, T. Yajima, H. Masuda, A. Odani, and O. Yamauchi, *Inorg. Chem.*, **36**, 5777 (1997).

26) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell Univ. Press, Ithaca (1960).

27) B. E. Fischer and H. Sigel, *J. Am. Chem. Soc.*, **102**, 2998

(1980).
28) S-H. Kim and R. B. Martin, *J. Am. Chem. Soc.*, **106**, 1707 (1984).
29) a) A. Odani and O. Yamauchi, *Bull. Chem. Soc. Jpn.*, **54**, 3773 (1981); b) A. Odani and O. Yamauchi, *Inorg. Chim. Acta*, **46**, L63(1981); c) A. Odani, S. Deguchi, and O. Yamauchi, *Inorg. Chem.*, **25**, 62 (1986).
30) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York (1969).