

Enantioselective Assembly Structures of Copper(II) and Zinc(II) Complexes with the 1:1 Condensation Products of Imidazole-4-carbaldehyde Derivatives and DL-Phenylalanine

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Copper(II) complexes with tridentate ligands H_2L^R (R = H, 2-Me, and 5-Me) derived from 1:1 condensation products of DL-phenylalanine and imidazole-4-carbaldehyde derivatives (imidazole-4-carbaldehyde, 2-methylimidazole-4-carbaldehyde, and 5-methylimidazole-4-carbaldehyde), $[CuClHL^H]$ (**1**), $[CuClHL^{2\text{-}Me}]$ (**2**), $[CuClHL^{5\text{-}Me}]\cdot MeOH$ (**3**), $[CuBrHL^H]$ (**4a** and **4b**), and $[CuBrHL^{2\text{-}Me}]$ (**5**), were prepared. Two types of crystals in the reaction vessel, **4a** and **4b**, were obtained in the reaction between $CuBr_2$ and H_2L^H. Their assembled structures were determined by single-crystal analysis. Except for **4b**, the complexes assumed a homochiral chain structure constructed by intrachain imidazole–carboxylato hydrogen bonds between the adjacent two molecules, and the adjacent chains are linked by interchain Cu–X (X = Cl or Br) interactions. **3** exhibited a shorter interchain Cu–X distance and crystallized in the acentrosymmetric space group $C222_1$ representing a spontaneous resolution (conglomerate), while **1**, **2**, **4a**, and **5** gave a stacking of the adjacent chains with opposite chiralities to give racemic crystals. **4b** assumed a homochiral chain structure constructed by a coordination bond between a copper(II) ion and an oxygen atom of the carboxyl group of the adjacent complex. A zinc(II) complex, $[ZnClHL^H]$ (**6**), showed a similar racemic crystal to that of **4b**.

The fields of crystal engineering and supramolecular chemistry have attracted much attention in the past two decades, where an assembly process of well-designed molecules plays an important role.[1] Chirality is positioned at the top of the stereo-structural classes, and the chiral assembly process is an important subject in chemistry.[2] Numerous studies have been devoted to elucidating the detailed mechanism of enantioselectivity. When a racemate aggregates and condenses, it can form the following: (1) a racemic crystal (also called a racemic compound or a true racemate, in which the two enantiomers are present in equal quantities in a well-defined arrangement within the crystal lattice); (2) a conglomerate (a mechanical mixture of crystals of the pure enantiomers); or (3) a racemic solid solution (a pseudoracemate).[3] The formation of a conglomerate is rare and most racemates (>90%) crystallize as racemic crystals. The factors governing conglomerate crystallization have been discussed for chiral organic compounds and metal complexes.[4] The molecular design of a conglomerate is very simple. If one can find a homochiral discrimination between neighboring chiral units and then the homochiral interaction can be extended to the three-dimensional lattice, the compound will be a conglomerate.[5] It can be a reasonable approach toward forming a conglomerate to begin by studying the chiral discrimination between the two neighboring units, and then to extend this to chiral one-dimensional, two-dimensional, and finally three-dimensional aggregation.

For the purpose of the molecular design of conglomerates, a self-assembly process involving a metal ion is especially attractive and useful, where the chiral discriminative interactions may arise from coordination bonds and/or hydrogen bonds, which are quite strong, selective, and directional. In our previous papers,[6] we have reported the chiral aggregation process for a copper(II) complex with methylbis{3-[(2-methylimidazol-4-yl)methyleneamino]propyl}amine $[Cu(H_2L_A)]^{2+}$ and a cobalt(III) complex with tris{2-[(imidazol-4-yl)methyleneamino}ethyl]ethyl}amine ($[Co(H_3L_B)]^{3+}$). Both metal complexes are chiral molecules with either a C (clockwise) or an A (anticlockwise) configuration, resulting from the screw coordination arrangement of the achiral ligand. Their deprotonated species, $[Cu(HL_A)]ClO_4$ and $[Co(H_{1.5}L_B)]Cl_{1.5}$ (i.e., $[Co^{III}(H_3L_B)][Co^{III}(L_B)]Cl_3$), were prepared by controlled deprotonation. In a crystal of $[Cu(HL_A)]ClO_4$,[6a] a homochiral 1D chain is formed by intermolecular imidazole–imidazolato hydrogen bonds. In a crystal of $[Co^{III}(H_3L_B)][Co^{III}(L_B)]Cl_3$,[6f] two components, $[Co^{III}(H_3L_B)]^{3+}$ and $[Co^{III}(L_B)]^0$, which have the same absolute configuration, are linked by imidazole–imidazolato hydrogen bonds to form a 2D puckered sheet structure and the sheets with the same chirality are stacked to give a homochiral crystal (conglomerate).

In this study, we have focused on the enantioselective assembly process of copper(II) complexes with tridentate Schiff-base ligands derived from the 1:1 condensation reaction of imidazole-4-carbaldehyde derivatives and DL-phenylalanine (H_2L^R), $[MXHL^R]$ (M = Cu and Zn; X = Cl and Br; R = H, 2-Me, and 5-Me) (Chart 1).[7] Since the complex contains imidazole and chiral amino acid moieties in the tridentate ligand, the intermolecular interactions[8] as well as the chiral discriminations may arise from coordination bonds and/or

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hydrogen bonds. Here we report enantioselective assembly structures of [CuClHL^{H}] (**1**), [CuClHL$^{2\text{-Me}}$] (**2**), [CuClHL$^{5\text{-Me}}$]·MeOH (**3**), [CuBrHL^{H}] (**4a**), [CuBrHL^{H}] (**4b**), [CuBrHL$^{2\text{-Me}}$] (**5**), and [ZnClHL^{H}] (**6**).

Results and Discussion

Synthesis and Characterization of Copper(II) and Zinc(II) Complexes. A tridentate ligand H_2L^{H} was prepared by the 1:1 condensation reaction of imidazole-4-carbaldehyde and DL-phenylalanine in a mixed solution of methanol and H_2O (2/1 by volume), and the resulting ligand solution was used for the synthesis of the metal complex without ligands isolation. Two other ligands, $H_2L^{2\text{-Me}}$ and $H_2L^{5\text{-Me}}$, were prepared by a similar synthetic method as for H_2L^{H} by the use of 2-methylimidazole-4-carbaldehyde and 5-methylimidazole-4-carbaldehyde, respectively, instead of imidazole-4-carbaldehyde. The chloro copper(II) complexes, [CuClHL^{H}] (**1**), [CuClHL$^{2\text{-Me}}$] (**2**), and [CuClHL$^{5\text{-Me}}$]·MeOH (**3**), were prepared by mixing each of the tridentate ligands and $CuCl_2 \cdot 2H_2O$ in a mixed solution of methanol and H_2O (2/1 by volume). On slow crystallization at room temperature, **1** and **2** were obtained as blue plate crystals, and **3** was obtained as blue needle crystals.

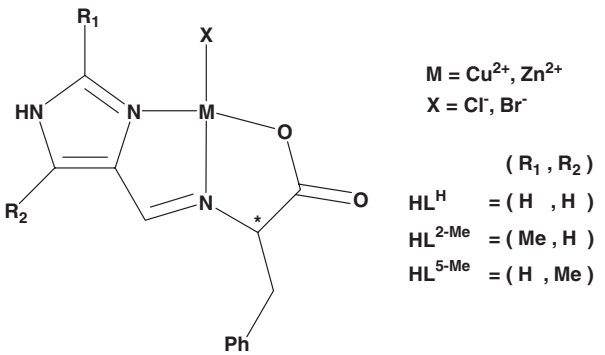

Chart 1.

The yields are around 30%, whose relatively small values are probably due to the high solubilities of the complexes in crystallization solvent. The yield was not changed by increasing the reaction scale (ca. 2 times large scale). The syntheses of bromo copper(II) complexes with the three ligands were attempted. In the reaction of $CuBr_2$ and H_2L^{H}, two types of crystals, [CuBrHL^{H}] (**4a**) and [CuBrHL^{H}] (**4b**), were obtained as blue rhombic and green plate-like crystals in the reaction vessel, and they were separated manually. [CuBrHL$^{2\text{-Me}}$] (**5**) was obtained as blue crystals, but [CuBrHL$^{5\text{-Me}}$] was obtained as thin needle crystals that were not suitable for X-ray analysis. A zinc(II) complex, [ZnClHL^{H}] (**6**) was prepared using zinc(II) chloride, in order to see the effect of the metal ion. The seven metal complexes obtained in this study, **1**, **2**, **3**, **4a**, **4b**, **5**, and **6**, showed satisfactory agreement of the C, H, and N elemental analytical data. Reflectance spectra were measured. The maxima in the visible region are given in the experimental section. On the basis of the characteristic IR bands, the seven complexes are divided into two groups. The first group of **1**, **2**, **3**, **4a**, and **5** showed two intense bands at ca. 1635 and 1670 cm^{-1}, assignable to the C=N stretching vibration of the Schiff-base ligand and the C=O stretching vibration of the carboxylato group of the DL-phenylalanine moiety, respectively.[9] On the other hand, the second group of **4b** and **6** showed bands at ca. 1640 and 1560 cm^{-1}, where the band assigned to the C=O stretch vibration around 1560 cm^{-1} was shifted to lower wavenumber because of the bridging structure.[9]

Structure of [Cu^{II}ClHL^{H}] (1). Tables 1 and 2 show the crystallographic data and relevant bond distances of chloro copper(II) complexes **1**, **2**, and **3**, respectively. Complex **1** crystallized in the centrosymmetric space group $P2_1/a$ (No. 14), indicating that two enantiomers of copper(II) complexes of the tridentate ligands consisting of the D- and L-phenylalanine moieties are contained in the unit cell. The molecular structure of **1** with the atom numbering scheme is shown in Figure 1. The copper(II) ion is coordinated by the

Table 1. Crystallographic Data for [CuClHL^{H}] (**1**), [CuClHL$^{2\text{-Me}}$] (**2**), and [CuClHL$^{5\text{-Me}}$]·MeOH (**3**)

	[Cu^{II}ClHL^{H}] (**1**)	[Cu^{II}ClHL$^{2\text{-Me}}$] (**2**)	[Cu^{II}ClHL$^{5\text{-Me}}$]·MeOH (**3**)
Formula	$C_{13}H_{12}N_3O_2ClCu$	$C_{14}H_{14}N_3O_2ClCu$	$C_{15}H_{18}N_3O_3ClCu$
Fw	341.26	355.28	387.32
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/a$ (No. 14)	$P2_1/a$ (No. 14)	$C222_1$ (No. 20)
a/Å	6.992(3)	6.843(3)	7.254(3)
b/Å	16.715(7)	16.727(7)	17.409(5)
c/Å	11.970(4)	12.671(5)	26.921(9)
β/°	94.17(1)	90.13(2)	
V/Å^3	1395.2(9)	1450(1)	3399(2)
T/K	296	296	296
Z	4	4	8
D_{calcd}/Mg m^{-3}	1.624	1.627	1.513
μ(Mo Kα)/cm^{-1}	1.759	1.696	1.458
Crystal size/mm^3	0.33 × 0.13 × 0.13	0.31 × 0.22 × 0.18	0.22 × 0.22 × 0.12
R[a)]	0.026	0.028	0.056
wR[b)]	0.070	0.074	0.141
S	1.012	1.041	1.012
$(\Delta/\rho)_{max,min}$/e Å^{-3}	0.72, −0.33	0.41, −0.39	1.34, −0.85
Flack parameter			0.03(2)

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $wR = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

Table 2. Relevant Coordination Bond Lengths/Å, Angles/° for [$CuClHL^{H}$] (**1**), [$CuClHL^{2\text{-}Me}$] (**2**), and [$CuClHL^{5\text{-}Me}$]·MeOH (**3**) at 296 K

		[$Cu^{II}ClHL^{H}$] (**1**)	[$Cu^{II}ClHL^{2\text{-}Me}$] (**2**)	[$Cu^{II}ClHL^{5\text{-}Me}$]·MeOH (**3**)
Cu–N(1)		1.998(1)	2.007(2)	1.981(4)
Cu–N(3)		1.962(1)	1.960(2)	1.942(4)
Cu–O(1)		1.946(1)	1.963(2)	1.965(4)
Cu–Cl(1)		2.2332(5)	2.2326(6)	2.244(2)
N(1)–Cu–O(1)		157.41(6)	158.98(7)	158.2(2)
N(1)–Cu–N(3)		80.89(6)	81.23(7)	81.6(2)
N(3)–Cu–O(1)		80.79(6)	81.37(7)	80.0(2)
N(1)–Cu–Cl(1)		101.47(4)	102.87(5)	98.0(1)
N(3)–Cu–Cl(1)		176.65(4)	175.15(5)	172.9(2)
O(1)–Cu–Cl(1)		96.36(4)	94.08(5)	98.8(1)
Intermolecular distances				
N(2)···O(1)		2.723(2)[a)]	2.810(2)[a)]	2.903(5)[c)]
Cu(1)···Cl(1)		2.8949(5)[b)]	2.8936(7)[b)]	2.737(2)[d)]
D–H···A distances				
N(2)–H···O(1)[a)]	D–H	0.950	0.950	
	H···A	1.784	1.870	
N(2)–H···O(1)[c)]	D–H			0.950
	H···A			1.957
D–H···A angles		169.1(2)	169.8(2)	173.1(5)

Symmetry operation to the latter atom. a) $1/2 - x$, $1/2 + y$, $2 - z$. b) $-x$, $-y$, $2 - z$. c) $3/2 - x$, $-1/2 + y$, $3/2 - z$. d) $2 - x$, y, $3/2 - z$.

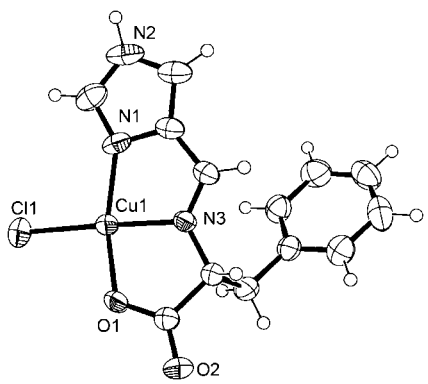

Figure 1. ORTEP drawing of [$CuClHL^{H}$] (**1**) with the selected numbering scheme at 296 K, where the thermal ellipsoids are represented at 50% probability level.

ClN_2O donor atoms of a chloride ion and an electronically mono-negative planar tridentate ligand derived from the 1:1 condensation reaction of imidazole-4-carbaldehyde and D- or L-phenylalanine (HL^{H}), where the carboxylato group of the DL-phenylalanine moiety is deprotonated but the imidazole group is not deprotonated. The coordination geometry around the copper(II) ion is described as square planar, with Cu–N(1) (imidazole) = 1.998(1) Å, Cu–N(3) (imine) = 1.962(1) Å, Cu–O(1) (carboxylato) = 1.946(1) Å, and Cu–Cl = 2.2332(5) Å. Figure 2 shows the crystal structure of **1**, representing the homochiral 1D assembled structure. The imidazole nitrogen atom N(2) of the copper(II) complex is hydrogen bonded to the carboxylato oxygen atom O(1)*1 of the adjacent copper(II) complex, that is related by a two-fold screw axis along the *b* axis (*1 represents a symmetry operation; $1/2 - x$, $1/2 + y$, $2 - z$) with the hydrogen-bond distance of N(2)···O(1)*1 = 2.723(2) Å. Because of the repeating hydrogen bonds, the complex forms a chain structure running along the *b* axis. It should be noted that the 1D chain is a homochiral chain consisting of one enantiomer of the D- or L-phenylalanine moiety, since within a chain, the adjacent copper(II) complexes are related by a two-fold screw axis. However, the crystal consists of chains with opposite chiralities, where the adjacent chains with opposite chiralities are doubly bridged by two chloride ions due to the core of Cu_2Cl_2. The Cu_2Cl_2 core has an inversion center with the dimensions Cu–Cl = 2.2332(5) Å and Cu–Cl*2 = 2.8949(5) Å (*2 represents a symmetry operation; $-x$, $-y$, $2 - z$). As shown in Figure 2, the heterochiral 2D network structure is constructed by two kinds of interaction, i.e., an intrachain imidazole–carboxylato hydrogen bond and a very weak interchain Cu–Cl*2 coordination bond, where the former interaction gives a homochiral chain and the latter gives a heterochiral stacking.

Substituent Effect on Chiral Aggregation: Structures of [$CuClHL^{2\text{-}Me}$] (2) and [$CuClHL^{5\text{-}Me}$]·MeOH (3). In order to answer the question "How does the methyl substituent of the imidazole moiety affect the structure assembly?," two complexes with the methyl group attached at different positions of the imidazole moiety, [$CuClHL^{2\text{-}Me}$] (**2**) and [$CuClHL^{5\text{-}Me}$]·MeOH (**3**), were subjected to X-ray structural analyses. Complex **2** crystallized in the monoclinic centrosymmetric space group $P2_1/a$ (No. 14) with similar cell parameters to **1** and assumes a similar crystal structure to **1**; that is, **2** assumes a

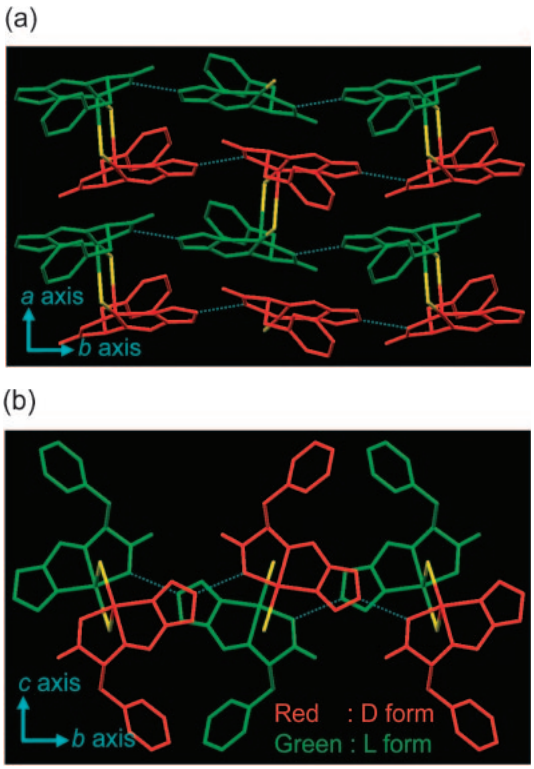

Figure 2. Heterochiral 2D network structure of [CuClHL^{H}] (**1**), where red- and green-colored molecules represent two enantiomers consisting of D- and L-phenylalanine moieties, respectively. The homochiral chain is constructed by intermolecular imidazole–carboxylato hydrogen bonds (blue dots). The adjacent chains with opposite chiralities are linked by interchain Cu–Cl^{*2} coordination bond (yellow, ^{*2} represents a symmetry operation of $-x$, $-y$, $2-z$). (a) Side view of the 2D structure and (b) top view of the 2D structure.

2D network structure consisting of homo-chiral 1D chains resulting from the imidazole–carboxylato hydrogen bonds and heterochiral stacking of the 1D chain with opposite chiralities because of the weak interchain Cu–Cl bridge.

On the other hand, complex **3** shows a different crystal structure from **1** and **2**. Complex **3** crystallized in the non-centrosymmetric space group $C222_1$ (No. 20), suggesting that a spontaneous resolution occurred. The molecular structure with the atom-numbering scheme is shown in Figure 3. The copper(II) ion assumes a square-planar coordination geometry with ClN_2O donor atoms and the coordination bond distances of Cu–N(1) (imidazole) = 1.981(4) Å, Cu–N(3) (imine) = 1.942(4) Å, Cu–O(1) (carboxylato) = 1.965(4) Å, and Cu–Cl = 2.244(2) Å, whose geometry is similar to that of **1** and **2**. Figure 4 shows the 2D network structure of **3**, in which the imidazole group of a copper(II) complex is hydrogen bonded to the carboxylato oxygen atom O(1)^{*3} (^{*3} represents a symmetry operation; $3/2-x$, $-1/2+y$, $3/2-z$) of the adjacent copper(II) complex with the distance of N(2)···O(1)^{*3} = 2.903(5) Å. Because of the repeating NH···O hydrogen bonds, the molecules with the same chirality produce a homochiral chain structure, the same as **1** and **2**. In the crystal, the adjacent chains with the same chirality (D-form) are stacked and linked

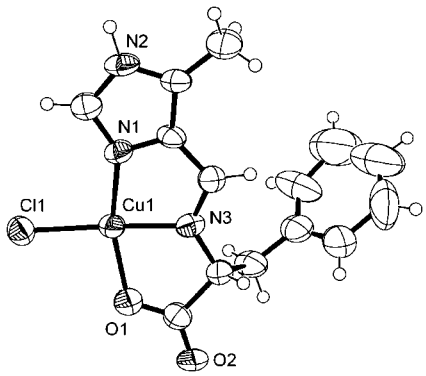

Figure 3. ORTEP drawing of [CuClHL$^{5\text{-Me}}$]·MeOH (**3**) with the selected atom-numbering scheme at 296 K, where the atom ellipsoids are 50% probability level.

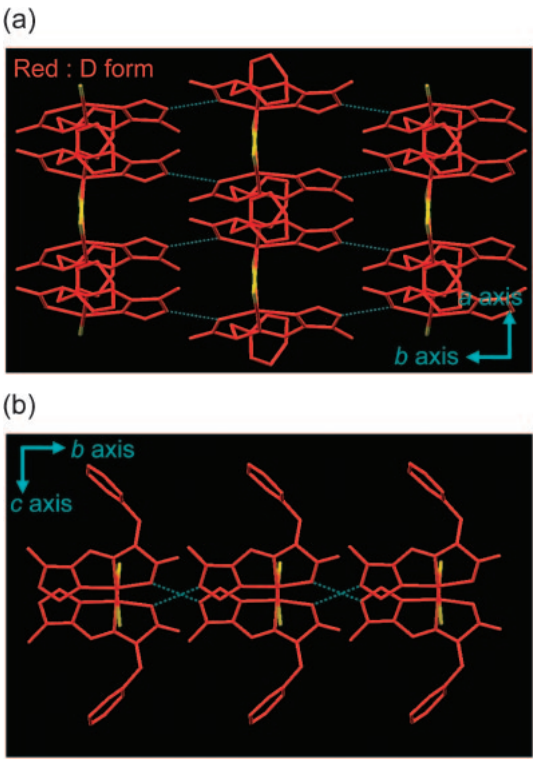

Figure 4. Homochiral 2D network structure of [CuClHL$^{5\text{-Me}}$]·MeOH (**3**), where the red-colored molecule represents one enantiomer consisting of the D-phenylalanine moiety. The homochiral chain is constructed by intrachain imidazole–carboxylato hydrogen bonds (blue dots). Adjacent chains with the same chirality are linked by the interchain coordination bond (yellow). (a) Side view of the 2D structure and (b) top view showing the stacking manner of the two adjacent chains.

by interchain Cu–Cl^{*4} coordination bonds with Cu–Cl^{*4} = 2.737(2) Å (^{*4} represents the symmetry operation; $2-x$, y, $3/2-z$) to produce a homochiral 2D network structure. It should be noted that the interchain Cu–Cl^{*4} distance of **3** is shorter than that of **1** (2.8949(5) Å) and **2** (2.8936(7) Å). It is also noteworthy that the crystal involves a methanol per the chemical formula as the crystal solvent and the methanol is

Table 3. Crystallographic Data for [CuBrHL^{H}] (**4a**), [CuBrHL^{H}] (**4b**), [CuBrHL$^{2\text{-Me}}$] (**5**), and [ZnClHL^{H}] (**6**)

	[CuBrHL^{H}] (**4a**)	[CuBrHL^{H}] (**4b**)	[CuBrHL$^{2\text{-Me}}$] (**5**)	[ZnClHL^{H}] (**6**)
Formula	$C_{13}H_{12}N_3O_2BrCu$	$C_{13}H_{12}N_3O_2BrCu$	$C_{14}H_{14}N_3O_2BrCu$	$C_{13}H_{12}N_3O_2ClZn$
Fw	385.71	385.71	399.73	343.09
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/a$ (No. 14)	$P2_1/c$ (No. 14)
a/Å	7.222(3)	12.103(6)	7.023(2)	12.051(7)
b/Å	16.697(5)	9.381(4)	16.856(5)	9.494(4)
c/Å	11.949(6)	13.035(7)	12.626(6)	12.877(6)
β/°	95.64(2)	106.81(2)	91.42(2)	105.15(2)
V/Å^3	1434.0(10)	1416.7(12)	1494.2(9)	1422.1(11)
T/K	296	180	296	296
Z	4	4	4	4
D_{calcd}/Mg m^{-3}	1.786	1.808	1.777	1.602
μ(Mo Kα)/cm^{-1}	4.3213	4.3740	4.1504	1.9181
Crystal size/mm^3	0.45 × 0.37 × 0.18	0.22 × 0.13 × 0.07	0.24 × 0.16 × 0.14	0.17 × 0.13 × 0.05
R[a)]	0.026	0.048	0.028	0.039
wR[b)]	0.061	0.081	0.048	0.047
S	1.034	0.907	1.022	1.007
$(\Delta/\rho)_{max,min}$/e Å^{-3}	0.66, −0.52	1.42, −1.28	0.67, −0.81	0.96, −1.00

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $wR = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

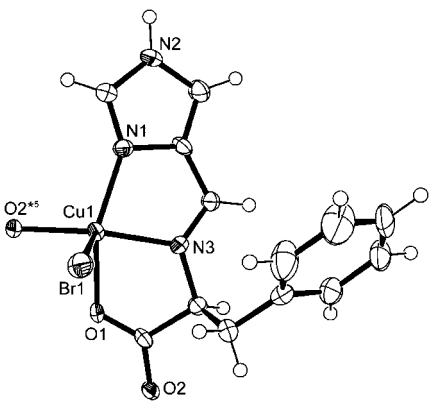

Figure 5. ORTEP drawing of [CuBrHL^{H}] (**4b**) with the atom-numbering scheme at 180 K, where the thermal ellipsoids are presented at 50% probability level.

hydrogen bonded to O(2) of the amino acid moiety with a distance of 3.00(2) Å. Although the elemental analyses of **3** and the large thermal parameters of the methanol molecule suggested the easy elimination of the crystal solvent, it is certain that the crystal solvent plays a role for the spontaneous resolution.

Effect of the Bridging Halogen Ion on the Assembly Structure: Structures of [CuBrHL^{H}] (4a), [CuBrHL^{H}] (4b), and [CuBrHL$^{2\text{-Me}}$] (5). In order to answer the question "How does the bridging halogen ion affect the structure assembly?," bromo complexes were prepared and studied. The complexes, [CuBrHL^{H}] (**4a**), [CuBrHL^{H}] (**4b**), and [CuBrHL$^{2\text{-Me}}$] (**5**), were subjected to X-ray structural analyses. Unfortunately, no crystals of [CuBrHL$^{5\text{-Me}}$] suitable for X-ray analysis were obtained. Tables 3 and 4 show the crystallographic data and relevant bond distances of bromo copper(II) complexes **4a**, **4b**, and **5**, respectively.

Complex **4a** crystallized in the monoclinic centrosymmetric space group $P2_1/a$ (No. 14) with similar cell parameters to **1** and **2**, and assumes a similar crystal structure to **1** and **2**. That is, **4a** assumes a square-planar coordination geometry with ClN_2O donor atoms and a 2D network structure consisting of a homochiral 1D chain resulting from the imidazole–carboxylato hydrogen bonds and heterochiral stacking of the 1D chains

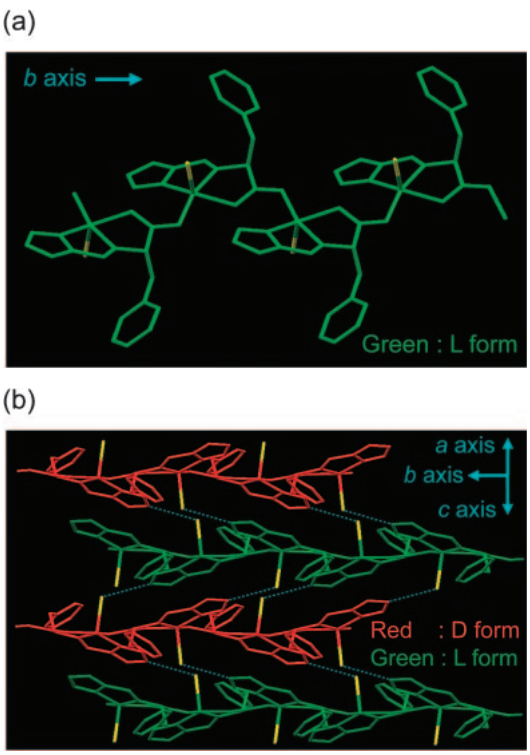

Figure 6. (a) Homochiral 1D chain structure of **4b** constructed from intermolecular Cu–O*5 coordination bonds (*5 represents the symmetry operation; $-x$, $-1/2 + y$, $3/2 - z$). (b) The heterochiral 2D network structure is constructed by interchain imidazole–Br^- hydrogen bonds.

Table 4. Relevant Coordination Bond Lengths/Å, Angles/° for [CuBrHL^{H}] (**4a**), [CuBrHL^{H}] (**4b**), [CuBrHL$^{2\text{-Me}}$] (**5**), and [ZnClHL^{H}] (**6**) at 296 K

	[CuBrHL^{H}] (**4a**)	[CuBrHL^{H}] (**4b**)	[CuBrHL$^{2\text{-Me}}$] (**5**)		[ZnClHL^{H}] (**6**)
Cu–N(1)	1.9917(16)	2.018(3)	2.0131(18)	Zn(1)–N(1)	2.101(2)
Cu–N(3)	1.9581(19)	1.957(3)	1.958(2)	Zn(1)–N(3)	2.091(2)
Cu–O(1)	1.9390(15)	2.040(2)	1.9581(16)	Zn(1)–O(1)	2.2082(19)
Cu–Br(1)	2.3721(3)	2.6043(9)	2.3678(4)	Zn(1)–Cl(1)	2.2607(12)
Cu–O(2)[a)]		1.929(2)		Zn(1)–O(2)[a)]	1.993(2)
N(1)–Cu–O(1)	158.19(8)	149.58(14)	160.13(8)	N(1)–Zn(1)–O(1)	139.01(9)
N(1)–Cu–N(3)	81.17(8)	80.90(14)	81.49(8)	N(1)–Zn(1)–O(2)[a)]	108.05(9)
N(3)–Cu–O(1)	81.00(7)	78.73(12)	81.71(8)	N(1)–Zn(1)–N(3)	77.50(9)
N(1)–Cu–Br(1)	100.29(6)	110.51(12)	102.56(6)	N(1)–Zn(1)–Cl(1)	113.58(8)
N(3)–Cu–Br(1)	175.84(5)	99.76(13)	174.23(5)	N(3)–Zn(1)–O(1)	72.80(7)
O(1)–Cu–Br(1)	96.70(5)	95.08(10)	93.52(5)	N(3)–Zn(1)–O(2)[a)]	146.65(10)
N(1)–Cu–O(2)[a)]		105.26(13)		N(3)–Zn(1)–Cl(1)	107.04(8)
N(3)–Cu–O(2)[a)]		162.61(15)		O(1)–Zn(1)–Cl(1)	101.84(6)
O(1)–Cu–O(2)[a)]		88.80(11)		O(1)–Zn(1)–O(2)[a)]	83.81(7)
Br(1)–Cu–O(2)[a)]		93.32(10)		Cl(1)–Zn(1)–O(2)[a)]	100.69(7)
Intermolecular distances					
N(2)···O(1)[b)]	2.724(2)		2.875(2)		
Cu(1)···Br(1)[c)]	3.0045(3)		3.0363(3)		
N(2)···Br(1)[d)]		3.304(3)		N(2)···Cl(1)[d)]	3.214(2)
D–H···A distances					
N(2)–H···O(1)[b)] D–H	0.950		0.950		
H···A	1.780		1.929		
N(2)···Br(1)[d)] D–H		0.950			0.950
H···A		2.367			2.279
D–H···A angles	172.0(2)	168.6(4)	173.4(2)		167.7(3)

Symmetry operation to the a) $-x, -1/2 + y, 3/2 - z$. b) $1/2 - x, 1/2 + y, 2 - z$. c) $-x, -y, 2 - z$. d) $x, -1/2 - y, 1/2 + z$.

with the opposite chiralities because of the weak interchain Cu···Br bridge (3.0045(3) Å).

On the other hand, **4b** assumes a different coordination geometry and a different assembly structure. The molecular structure of **4b** with the selected atom-numbering scheme and crystal structure are shown in Figures 5 and 6, respectively. As shown in Figure 5, a Br^{-} ion coordinates to a copper(II) ion, but it is not in the plane of the tridentate ligand. An oxygen atom O(2)*5 (*5 represents the symmetry operation; $-x$, $-1/2 + y$, $3/2 - z$) of the amino acid moiety of the adjacent copper(II) complex coordinates to the copper(II) ion with a distance of O(2)*5–Cu(1) = 1.929(2) Å and occupies one of the four equatorial coordination sites. The copper(II) ion has a square-pyramidal coordination geometry with BrN_2O_2 donor atoms, where the axial site is occupied by a Br^{-} ion and the equatorial sites are occupied by a tridentate ligand and an oxygen atom of the adjacent molecule. For that reason, the IR band of C=O stretching vibration appeared at the lower wavenumber. As a result of the repeating coordination bonds of O(2)*5–Cu(1), the complex produces a polynuclear chain structure running along the b axis, where the bridging conformation of the carboxylato group of the amino acid moiety is a triatomic syn–anti type. Within a chain the two adjacent copper(II) complexes are related by a two-fold screw axis so that the complexes within a chain involve only one enantiomer of the D- or L-phenylalanine residue. However, the chains with opposite chiralities are stacked alternately to give a racemic crystal, where an interchain hydrogen bond with N(2)···Br*6 = 3.304(3) Å (*6 represents the symmetry operation; x, $-1/2 - y$, $1/2 + z$) is operating to produce a heterochiral 2D network structure.

Effect of the Central Metal Ion on the Assembly Structure: Structure of [ZnClHL^{H}] (6). In order to answer the question "How does the central metal ion affect the structure assembly?," a zinc(II) complex, [ZnClHL^{H}] (**6**) was subjected to an X-ray analysis. Complex **6** exhibited the same features in the IR bands and crystallized in the monoclinic centrosymmetric space group $P2_1/c$ (No. 14) with similar cell parameters to those of **4b**. The molecular structure and the crystal structure are shown in Figures 7 and 8, respectively. Zinc(II) ion has a pentacoordinated geometry with a tridentate ligand and chloride ion, and an amino–carboxylato oxygen atom of the adjacent molecule. The coordination geometry is better described as a trigonal bipyramid than a square pyramid, in comparison with that of **4b**. The complex assumes a polynuclear chain structure constructed by the intermolecular coordination bonds running along the b axis, where within a chain the two adjacent zinc(II) complexes are related by a two-

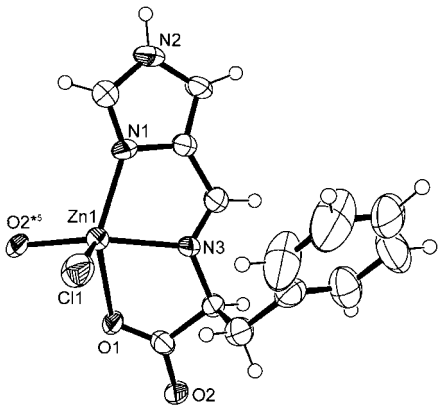

Figure 7. ORTEP drawing of [ZnClHL^{H}] (**6**) with the selected atom numbering scheme at 296 K, where the atom ellipsoids are 50% probability level.

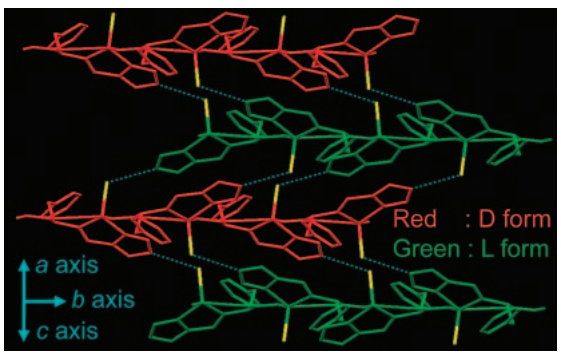

Figure 8. Homochiral 1D chain structure of **6** constructed by Zn–O^{*5} coordination bond and racemic 2D network structure. The heterochiral 2D network structure is constructed by interchain imidazole–Cl^{-} hydrogen bonds.

fold screw axis and have the same chirality. However, the adjacent two chains with opposite chiralities are linked by the interchain N(2)···Cl^{*6} (^{*6} represents the symmetry operation; x, $-1/2-y$, $1/2+z$) hydrogen bond with N(2)···Cl^{*6} = 3.214(2) Å to produce a racemic 2D network structure.

Magnetic Properties of 3 and 4b. Compounds **3** and **4b** were subjected to the magnetic studies, as the representative compounds. The temperature dependences of the magnetic susceptibilities in the temperature range of 2.0–300.0 K under the external magnetic field of 0.5 T and the field dependence of the magnetization at 2.0 K from 0 to 5 T were measured. The temperature dependences of $\chi_A T$ vs. T for **3** and **4b** are essentially similar to each other. The $\chi_A T$ value at the higher temperature region (>ca. 20 K) is close to the calculated value of 0.375 $cm^3\,K\,mol^{-1}$ expected for one Cu^{II} ($S = 1/2$) ion and decreases abruptly to at the lowest temperature (0.17 $cm^3\,K\,mol^{-1}$ at 2 K for **3**; 0.22 $cm^3\,K\,mol^{-1}$ at 2 K for **4b**). The field dependence of the magnetization at 2.0 K was plotted in Figure 9 in the form of $M/N\beta$ vs. H and compared with the Brillouin functions calculated for the isolated copper(II) molecule ($S_{Cu} = 1/2$). Both magnetization data are lower than the calculated Brillouin function of $g = 2.00$ and $S = 1/2$, suggesting an operation of antiferromagnetic coupling. The magnetization of **3** is much lower than that of **4b**. Compound **3**

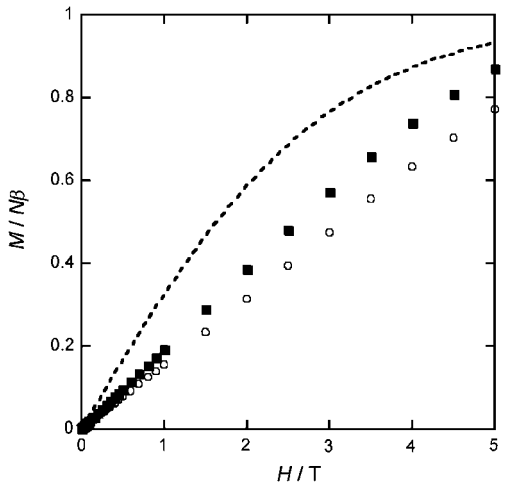

Figure 9. Field dependence of the magnetization of M at 2 K as a function of the applied magnetic field H for **3** (○) and **4b** (■). The broken dotted line represents the theoretical curves for the Brillouin functions for Cu^{II} ion $S = 1/2$ and $g = 2.00$.

can be described as that di-μ-chloro dinuclear copper(II) species are bridged by hydrogen bonds of inter-dimer imidazole–amino hydrogen bonds to form a 2D network structure. The magnetic data suggest that a weak antiferromagnetic interaction at di-μ-chloro dinuclear copper(II) species is predominant at 2 K. Compound **4b** is described as a carboxylato-bridged copper(II) 1D chain with tri-atomic syn–anti bridging conformation, whose chains are linked by interchain imidazole–Br^{-} hydrogen bonds to form 2D network structure. A number of one-dimensional (1D) carboxylato-bridged copper(II) complexes has been synthesized and their magnetic properties have been extensively studied.[10] In these complexes, a carboxylato group can assume many types of bridging conformations, such as triatomic syn–syn, anti–anti, and syn–anti types. It is known that the 1D copper(II) complexes with syn–anti bridging conformation assume weak ferro- or antiferro-magnetic interaction between the adjacent Cu^{II} centers to give a ferromagnetic or antiferromagnetic chain. The present complex **4b** did not show apparent character of a 1D ferromagnetic chain, probably due to the weak magnetic interaction within a chain and co-existence of weak inter- and intra-chain magnetic interactions, demonstrating that the magnetic interaction is too weak to detect the character of the 1D chain. As a whole, the magnetic data are not so informative to distinguish the difference of the network structures.

Concluding Remarks

Copper(II) and zinc(II) complexes with the tridentate ligands H_2L^{R} of 1:1 condensation products of DL-phenylalanine and imidazole-4-carbaldehyde derivatives (imidazole-4-carbaldehyde, 2-methylimidazole-4-carbaldehyde, and 5-methylimidazole-4-carbaldehyde), [CuClHL^{H}] (**1**), [CuClHL$^{2\text{-Me}}$] (**2**), [CuClHL$^{5\text{-Me}}$]·MeOH (**3**), [CuBrHL^{H}] (**4a** and **4b**), [CuBrHL$^{2\text{-Me}}$] (**5**), and [ZnClHL^{H}] (**6**), were prepared, since the imidazole and chiral amino-acid moieties of the complexes can act as functional groups to construct an intermolecular network structure. **1**, **2**, **3**, **4a**, and **5** assumed a homochiral

chain structure constructed by intrachain imidazole–carboxylato hydrogen bonds, and **4b** and **6** assumed a homochiral chain constructed by intermolecular coordination bonds. Among seven complexes, only **3** crystallized in the acentrosymmetric space group $C222_1$ representing a spontaneous resolution (conglomerate). Spontaneous resolution is achieved by three-dimensional homo-chiral assembling of chiral molecules. In order to realize a spontaneous resolution on the basis of a rational molecular design, we have examined step-wise processes toward 3D homo chiral assembly,[5a,6c,7] that is, (1) intermolecular homo-chiral recognition between adjacent two chiral molecules, (2) 1D homo-chiral chain extended by the homochiral interaction between the two molecules, (3) 2D homo-chiral layer constructed by homo-chiral assembly between the chains, and (4) 3D homo-chiral assembly in the crystal lattice. Although only one of the seven complexes **3** is successfully displayed spontaneous resolution, all complexes showed 1D homo-chiral aggregations, where one type of complexes **1**, **2**, **3**, **4a**, **5**, and **6** is connected by the hydrogen bonds and another type of complex **4b** is connected by coordination bonds. It is noted that this molecular system is a good system to reach a spontaneous resolution by step-wise process and to know the detailed structural factors toward spontaneous resolution.

Experimental

General and Materials. All chemicals and solvents were obtained from Tokyo Kasei Co., Ltd., and Wako Pure Chemical Industries, Ltd. These were of reagent grade and were used for the syntheses without further purification. All the synthetic procedures were carried out in an open atmosphere.

Tridentate Ligands H_2L^R (R = H, 2-Me, and 5-Me). The tridentate ligands H_2L^R (R = H, 2-Me, and 5-Me) were prepared by the 1:1 condensation reactions of DL-phenylalanine and either imidazole-4-carbaldehyde, 2-methylimidazole-4-carbaldehyde, and 5-methylimidazole-4-carbaldehyde, respectively, in a mixed solution of methanol and water (2/1 by volume) on a hot plate for 30 min.

[CuXHL^R] (X = Cl and Br; R = H, 2-Me, and 5-Me) 1, 2, 3, 4a, 4b, and 5. The synthetic procedures for all of the copper(II) complexes with the tridentate ligands are very similar to each other and the synthesis of [CuClHL^H] (**1**) is exemplified in detail. The resulting ligand solutions were used for the syntheses of the copper(II) complexes without the isolation of the ligands. The tridentate ligand H_2L^H was prepared by the 1:1 condensation reaction of DL-phenylalanine (0.083 g, 0.5 mmol) and imidazole-4-carbaldehyde (0.048 g, 0.5 mmol), in a mixed solution of methanol (10 mL) and water (5 mL) on a hot plate for 30 min. To a solution of the ligand (0.5 mmol) was added a solution of $CuCl_2 \cdot 2H_2O$ (0.085 g, 0.5 mmol) in methanol (5 mL). The mixture was warmed and stirred for 30 min and then filtered. The filtrate was allowed to stand for several days, during which time crystals precipitated. They were collected by suction filtration, washed with methanol and dried.

[CuClHL^H] (1): Anal. Found: C, 45.99; H, 3.56; N, 12.30%. Calcd for [CuClHL^H] = $C_{13}H_{12}N_3O_2ClCu$: C, 45.75; H, 3.55; N, 12.31%. IR (KBr disk): $\nu_{C=N}$ 1635.8 cm^{-1}; $\nu_{C=O}$ 1674.6 cm^{-1}. λ_{max}(solid) 469 nm.

[CuClHL$^{2\text{-Me}}$] (2): Anal. Found: C, 47.47; H, 4.19; N, 11.80%. Calcd for [CuClHL$^{2\text{-Me}}$] = $C_{14}H_{14}N_3O_2ClCu$: C, 47.33; H, 3.97; N, 11.83%. IR (KBr disk): $\nu_{C=N}$ 1632.3 cm^{-1}; $\nu_{C=O}$ 1670.2 cm^{-1}. Yield 34%

[CuClHL$^{5\text{-Me}}$] (3): Crystal solvent MeOH is eliminated in air to give the desolvated complex. Anal. Found: C, 47.35; H, 4.17; N, 11.72%. Calcd for [CuClHL$^{5\text{-Me}}$] = $C_{14}H_{14}N_3O_2ClCu$: C, 47.33; H, 3.97; N, 11.83%. IR (KBr disk): $\nu_{C=N}$ 1638.4 cm^{-1}; $\nu_{C=O}$ 1665.2 cm^{-1}. Yield 22%

[CuBrHL^H] (4a): Anal. Found: C, 40.69; H, 3.20; N, 10.93%. Calcd for [CuBrHL^H] = $C_{13}H_{12}N_3O_2BrCu$: C, 40.48; H, 3.14; N, 10.89%. IR (KBr disk): $\nu_{C=N}$ 1636.8 cm^{-1}; $\nu_{C=O}$ 1676.0 cm^{-1}. λ_{max}(solid) 474 nm.

[CuBrHL^H] (4b): Anal. Found: C, 40.52; H, 3.27; N, 10.96%. Calcd for [CuBrHL^H] = $C_{13}H_{12}N_3O_2BrCu$: C, 40.48; H, 3.14; N, 10.89%. IR (KBr disk): $\nu_{C=N}$ 1639.5 cm^{-1}; $\nu_{C=O}$ 1559.2 cm^{-1}. λ_{max}(solid) 484 nm.

[CuBrHL$^{2\text{-Me}}$] (5): Anal. Found: C, 41.68; H, 3.49; N, 10.29%. Calcd for [CuBrHL$^{2\text{-Me}}$] = $C_{14}H_{14}N_3O_2BrCu$: C, 42.07; H, 3.53; N, 10.51%. IR (KBr disk): $\nu_{C=N}$ 1635.8 cm^{-1}; $\nu_{C=O}$ 1668.6 cm^{-1}. λ_{max}(solid) 487 nm.

[ZnClHL^H] (6). To a solution of the ligand (0.5 mmol) was added a solution of $ZnCl_2$ (0.068 g, 0.5 mmol) in methanol (5 mL). The mixture was warmed and stirred for 30 min and then filtered. The filtrate was allowed to stand for several days, during which time crystals precipitated. They were collected by suction filtration, washed with methanol and dried. Anal. Found: C, 45.84; H, 3.86; N, 12.39%. Calcd for [ZnClHL^H] = $C_{13}H_{12}N_3O_2ClZn$: C, 45.51; H, 3.53; N, 12.25%. IR (KBr disk): $\nu_{C=N}$ 1647.8 cm^{-1}; $\nu_{C=O}$ 1673.1 cm^{-1}.

Physical Measurements. C, H, and N elemental analyses were performed by Miss. Kikue Nishiyama at the Center for Instrumental Analysis of Kumamoto University. Infrared spectra were recorded at room temperature using a Nicolet Avatar 370 DTGS (Thermo Electron Corporation) spectrometer with samples in KBr disks. Magnetic data were measured by a MPMS5 SQUID susceptometer (Quantum Design). Magnetic susceptibilities were measured in a 2–300 K temperature range under an applied magnetic field of 0.5 T. Magnetization at 2 K was measured from 0 to 5 T. The apparatus was calibrated with palladium metal. Corrections for diamagnetism were applied by using Pascal's constants. Reflectance spectra were measured on a Shimadzu UV-2450 UV–visible spectrophotometer.

Crystallographic Data Collection and Structure Determination for [MXHL^R] (M = Cu and Zn; X = Cl and Br; R = H, 2-Me, and 5-Me) 1–6. All measurements were made on a Rigaku RAXIS RAPID-F imaging plate area detector with graphite monochromated Mo Kα radiation (λ = 0.71075 Å). The data were collected to a maximum 2θ value of 55°. The data except for **4b** were collected at 296 K, while the data of **4b** were collected at 180 K. Absorption corrections were applied. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and expanded using the Fourier technique.[11] The structures were refined on F^2 full-matrix least-squares method with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were fixed in their calculated positions and refined by using a riding model. The atomic scattering factors and anomalous dispersion terms were taken from the standard compilation.[12] All calculations were performed by using the Crystal Structure crystallographic software package.[13] The crystal data collection and refinement parameters are given in Tables 1 and 3. X-ray crystallographic files in CIF format for seven compounds are deposited at the Cambridge Crystallographic Data Centre at the deposit numbers CCDC 299424, 604561, and 714836–714840.

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