DOI: 10.1002/ejic.200600967

Supramolecular Helical Architectures Dictated by Folded and Extended Conformations of the Amino Acid in Ternary Cu^{II}/Diamine/Racemic Amino Acid Complexes

Palani Sivagnana Subramanian,*[a] Eringathodi Suresh,[a] and Luigi Casella*[b]

Keywords: Helicates / Self-assembly / Copper / Chiroptical properties / Amino acids

The ternary Cu^{II} complexes [Cu(D,L-phe)(bpy)]·(ClO_4) (**1**), [Cu(D,L-phe)(phen)(H_2O)]·ClO_4·H_2O (**2**), and [Cu(L-phe)(bpy)(H_2O)]·ClO_4·H_2O (**3**) (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline) adopt helical structures in the crystal state, as determined by an X-ray structural analysis. The supramolecular helical assembly of these complexes was also investigated by single-crystal X-ray crystallography. The complexes derived from racemic amino acids (**1** and **2**) undergo spontaneous resolution in the solid state to form separate helical chains of the ternary complex that carry a single enantiomer of the amino acid. In the case of complex **1**, the two helical chains resulting from the L- and D-phe complexes bear opposite chirality, which means that the bulk crystalline sample is racemic. In contrast, the two helical chains generated by L- and D-phe complexes in **2** have the same twist and pack together in a right-handed assembly. The (*P*)/(*M*) handedness of the helical chains is dictated by the conformational chirality (λ/δ) of the chelate rings of the D/L-amino acids.

Introduction

Compounds that are achiral in nature but gain chiroptical properties upon formation of supramolecular helical architectures have received a great deal of interest in recent years.[1] A number of ternary Cu^{II}/diamine (DA) complexes with optically active D- and L-amino acids (AA), where the latter residues can be present in folded and extended conformations, are known, and their optical properties in solution have been studied extensively.[2–4] Many of the investigations on such [Cu^{II}(DA)(AA)][5–9] complexes reported so far have focused mainly on structure/reactivity correlations and conformational studies; no correlation between their structural architecture and solid-state optical properties has been reported. Inorganic metallohelicates[10] are known to have interesting chiroptical properties. Intensive efforts to amplify the chiroptical properties obtained by supramolecular helicity by introducing various chiral residues or molecules such as chiral spacers,[11,12] amino acids,[13,14] and chiragens[14] into the helical skeleton have been made by a number of researchers, including Raymond et al.[15] and Albrecht et al.[16] Recent articles by Kuroda et al.,[1a,17] however, have explored the chiroptical properties exhibited by achiral complexes. The self-assembled, single-stranded supramolecular architecture of ternary [Cu^{II}(DA)(AA)] complexes obtained from a simple one-pot reaction that contain the amino acid in their helical skeleton inspired us to investigate their optical behavior. In the structure of the complexes [Cu(D,L-phe)(bpy)]·ClO_4 (**1**), [Cu(D,L-phe)(phen)(H_2O)]·ClO_4·H_2O (**2**), and [Cu(L-phe)(bpy)(H_2O)]·ClO_4·H_2O (**3**) that we describe here (bpy = 2,2′-bipyridyl; phen = 1,10-phenanthroline), the difference in the orientation of the phenylalanine side chain results in folded and extended conformations of the amino acid chelate ring that lead to noncovalently propagated supramolecular helical architectures. Folded and extended forms of ternary aromatic amino acid complexes have been reported by many researchers,[2,5,7–9] and here we show how these conformations can influence the helicity of the polymeric structure of the ternary complexes. Complexes **1** and **2**, which contain racemic phenylalanine, undergo spontaneous resolution in the crystalline state and their different supramolecular helical structures result in interesting differences in chiroptical properties in the solid state. The potential sources of optical activity in the ternary complexes **1**–**3** are discussed in terms of the Δ/Λ configuration of the Cu^{II} chromophoric units, the supramolecular helicity (*P*)/(*M*), and the λ/δ conformational chirality of the nonplanar D/L-amino acid chelate rings.

[a] Analytical Science Division, Central Salt and Marine Chemicals Research Institute,
Gijubhai Badhegha Marg, Bhavnagar, 364002, Gujarat, India
Fax: +91-278-256-6970
E-mail: siva@csmcri.org
[b] Dipartimento di Chimica Generale, Università di Pavia,
Via Taramelli 12, 27100 Pavia, Italy
Fax: +39-0382-528-544
E-mail: bioinorg@unipv.it

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

Results and Discussion

Crystal Structures and Molecular Association

ORTEP diagrams of complexes **1**–**3** with the atom numbering schemes are given in Figure 1. A summary of the crystallographic data is given in the Experimental Section and selected bond lengths and angles for **1**–**3** are given in Table 1. The Cu^{II} ions in complexes **1**–**3** possess a distorted square-pyramidal geometry where the base of the square pyramid is constituted by the pyridyl nitrogen atoms of the heterocyclic diamines and the NH_2 and CO_2 groups of the amino acids (L-, D-phe). The fifth axial ligand is different and consists of a carboxylate oxygen atom in **1** and a water molecule in **2** and **3**. The long Cu^{II}–carboxylate oxygen bonds [Cu1–O4 2.274(2), Cu2–O2 2.261(2) Å] formed by O2 and O4 of phenylalanine in **1** define a folded single-stranded helical, cationic polymeric chain along the *a* axis. The carboxylate oxygen atom O2 coordinated to Cu(2) possesses an additional weak short contact with one of the two bipyridyl nitrogen atoms (O2–N4 2.910 Å) that may have some significance for the helical arrangement. The helical chain is constructed from –Cu1–OCO–Cu2– bonds with Cu^{II} centers sitting alternatively at distances of 5.883 and 5.864 Å. The aromatic rings of the amino acids C13 to C18 and C32 to C37 adopt only a folded conformation in complex **1** and are oriented almost parallel to the bpy rings, with a slight deviation of 2.74 and 6.99°, respectively, from the mean plane, which facilitates strong intra- and intermolecular stacking interactions (Figure 2A).

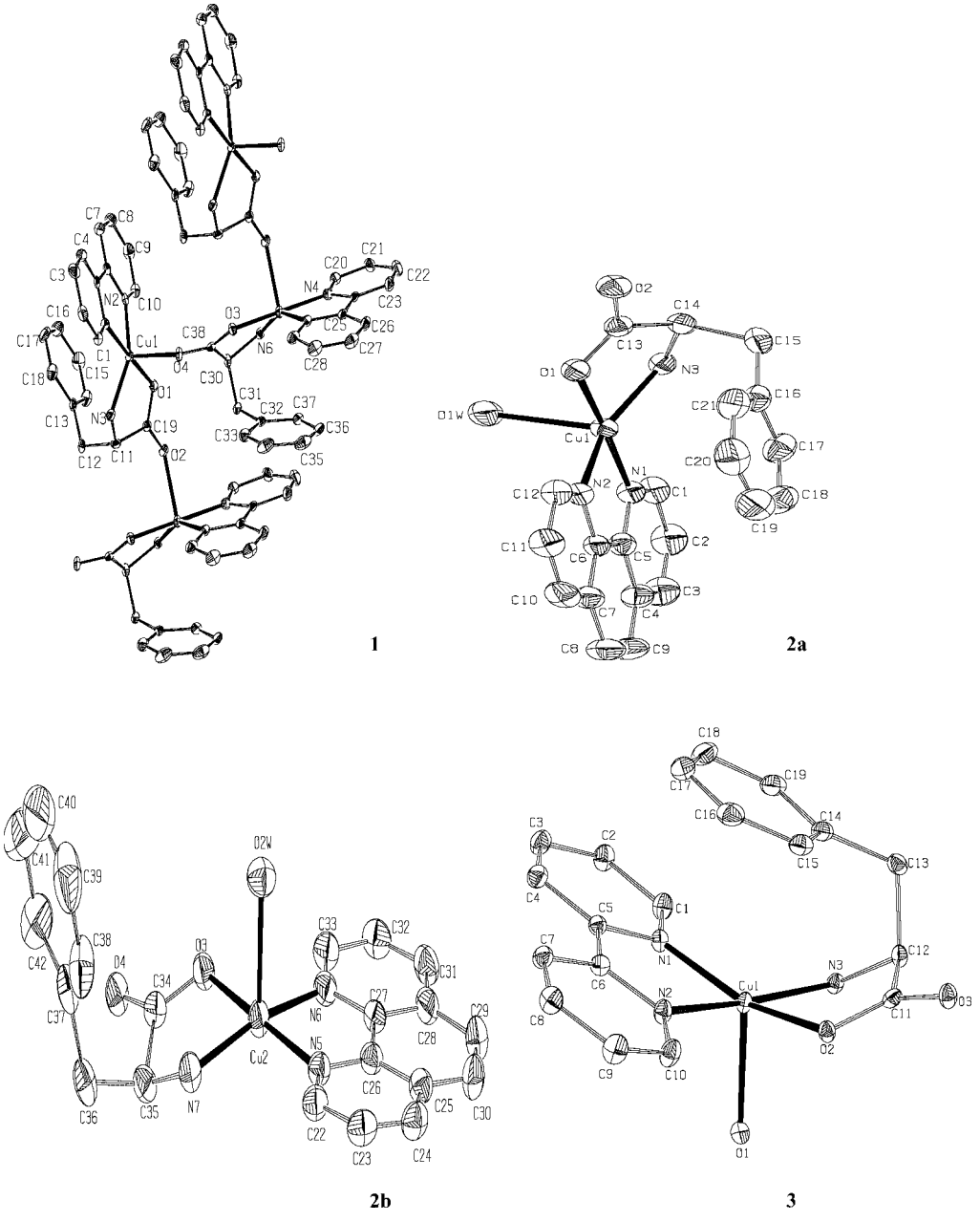


Figure 1. ORTEP diagrams of the structures of complexes **1**–**3**.

Table 1. Selected bond lengths [Å]and bond angles [°] for complexes **1**–**3**.[a]

	1		
Cu1–O1	1.9432	Cu2–O3	1.9462
Cu1–N2	1.9883	Cu2–N6	1.9902
Cu1–N3	1.9932	Cu2–N4	1.9923
Cu1–N1	1.9953	Cu2–N5	1.9953
Cu1–O4	2.2742	Cu2–O2#1	2.2612
O1–Cu1–N2	96.0810	O3–Cu2–N6	84.479
O1–Cu1–N3	84.419	O3–Cu2–N4	177.7310
N2–Cu1–N3	151.8610	N6–Cu2–N4	97.6710
O1–Cu1–N1	177.549	O3–Cu2–N5	96.3010
N2–Cu1–N1	81.5610	N6–Cu2–N5	150.9910
N3–Cu1–N1	97.9910	N4–Cu2–N5	81.4611
O1–Cu1–O4	94.588	O3–Cu2–O2#1	94.198
N2–Cu1–O4	107.939	N6–Cu2–O2#1	103.079
N3–Cu1–O4	100.059	N4–Cu2–O2#1	86.099
N1–Cu1–O4	85.529	N5–Cu2–O2#1	105.789
	2		
Cu1–O1	1.952617	Cu2–O3	1.936417
Cu1–N3	2.0042	Cu2–N5	1.9972
Cu1–N2	2.0072	Cu2–N6	2.0052
Cu1–N1	2.0102	Cu2–N4	2.0122
Cu1–O1w	2.2852	Cu2–O2w	2.3512
O1–Cu1–N3	83.748	O3–Cu2–N5	94.488
O1–Cu1–N2	93.728	O3–Cu2–N6	83.088
N3–Cu1–N2	159.669	N5–Cu2–N6	167.9510
O1–Cu1–N1	176.058	O3–Cu2–N4	176.538
N3–Cu1–N1	100.099	N5–Cu2–N4	82.439
N2–Cu1–N1	82.358	N6–Cu2–N4	99.629
O1–Cu1–O1w	86.0810	O3–Cu2–O2w	95.438
N3–Cu1–O1w	100.1310	N5–Cu2–O2w	97.0910
N2–Cu1–O1w	99.819	N6–Cu2–O2w	94.8911
N1–Cu1–O1w	94.1410	N4–Cu2–O2w	86.538
	3		
Cu1–O2	1.972916	Cu1–N2	1.980919
Cu1–N3	1.9992	Cu1–N1	2.001919
Cu1–O1	2.301414		
O2–Cu1–N2	92.068	O2–Cu1–N3	82.396
N2–Cu1–N3	171.508	O2–Cu1–N1	160.797
N2–Cu1–N1	81.087	N3–Cu1–N1	102.148
O2–Cu1–O1	90.736	N2–Cu1–O1	98.247
N3–Cu1–O1	88.307	N1–Cu1–O1	107.957

[a] Symmetry operation for atom #1 = $x-1$, y, z.

Complex **2** differs from **1** and **3** by crystallizing with two independent molecules in the asymmetric unit; one contains the D isomer of the amino acid in the folded form only (henceforth referred to as **2a**), while the other contains only the L-amino acid in an extended form (henceforth referred to as **2b**). Similar folded and extended conformations have already been reported in analogous ternary copper(II) complexes such as [Cu(L-trypO)(phen)]$^+$,[18] [Cu(L-phe)(phen)Cl]·3H_2O,[8] [Cu(L-*o*-Me-phe)(phen)(H_2O)]ClO_4,[5c] [Cu(L-NH_2Phe)(bpy)]·NO_3·H_2O,[8] and [Cu(L-tyr)(phen)(H_2O)]·ClO_4·1.5H_2O,[8] etc. We have also recently reported a folded conformation of L-phe in the ternary complex [Cu(L-phe)(bpy)(H_2O)]·ClO_4.[9] The coordination around Cu^{II} remains almost the same for both **2a** and **2b**, although the phenylalanine side chain varies somewhat in its orientation. The apical coordination of the Cu^{II} square pyramid is fulfilled by long bonds with water molecules [Cu1–O1w 2.285 (**2a**), Cu2–O2w 2.351 Å (**2b**)] in both cases, while the square base resembles that present in complexes **1** and **3**.

Similar to complex **1**, the phenyl ring of D-phe in **2a** is almost parallel to the phenanthroline ring (tilt angle of 5.29°) and forms a folded isomer. However, the phenyl moiety of L-phe in **2b** is inclined towards the perpendicular of the phenanthroline ring (tilt angle of 71.96°) to yield an extended isomer. The folded and extended isomers **2a** and **2b**, respectively, in Figure 2 are packed with the phenyl ring of the amino acid pair pointing in opposite directions and give effective π···π stacking interactions, as shown in Figure 2D. The offset inter- and intramolecular π···π stacking interactions between the phenyl rings of the bpy/phen ligands and the aromatic rings of the amino acids in complexes **1** and **2** are depicted in Figure 2; the stacking distances are given in the figure caption. The weak π···π interactions clearly play a significant role: the aromatic ring of the folded phenylalanine causes the intramolecular π···π stacking interaction and that of the extended form facilitates the intermolecular π···π stacking interaction, as indicated by the double-headed arrows in Figure 2. Further, the phenanthroline units of the folded and extended forms generate interhelical π···π stacking through the centroids [Cg_3(ext)···Cg_2(fold) 3.539 Å] of their aromatic rings.

Supramolecular Helical Association and Chirality

The stereochemical descriptors (*P*) or (*M*) can be assigned to the helical assemblies in **1**–**3** depending on the clockwise or anticlockwise bias of the helical strand, respectively. It is noteworthy that the supramolecular packing in complexes **1**–**3** generates a one-dimensional inner-sphere helical arrangement running through the metal centers by a combination of weak inter- and intramolecular π···π stacking and hydrogen-bonding interactions, as shown in Figure 2. An imaginary helical axis drawn between the metal centers along the *a* axis is shown in Figure 3. In all cases the bipyridyl ligand and the phenyl ring of the amino acid that projects outwards revolve around the helical axis with good intra- and intermolecular π···π stacking interactions. The intramolecular helical structure running through the Cu1–OCO–Cu2 strands in complex **1** contains only folded phenylalanine isomers. As expected, therefore, the arrangement of the two polymeric helical chains containing the D- and L-amino acids in this complex occurs through the formation of alternately packed (*P*) and (*M*) helices, as shown in Figure 3A.

The coordinated O1w and O2w molecules of the folded and extended conformers in complex **2** propagate the hydrogen-bonded helical architecture through Cu1–O1w···O2CO1–Cu1 and Cu2–O2w···O4CO3–Cu2 bonds, respectively, diagonal to the *ac* plane. The O1w and O2 (carboxylate oxygen) atoms of the adjacent molecular units of the folded form are interconnected by hydrogen bonds (O1w···O2 2.747 Å) to form a single-stranded helical chain. Similarly, the O2w and O4 (carboxylate oxygen) atoms (O2w···O4 2.857 Å) of the extended form are interlinked

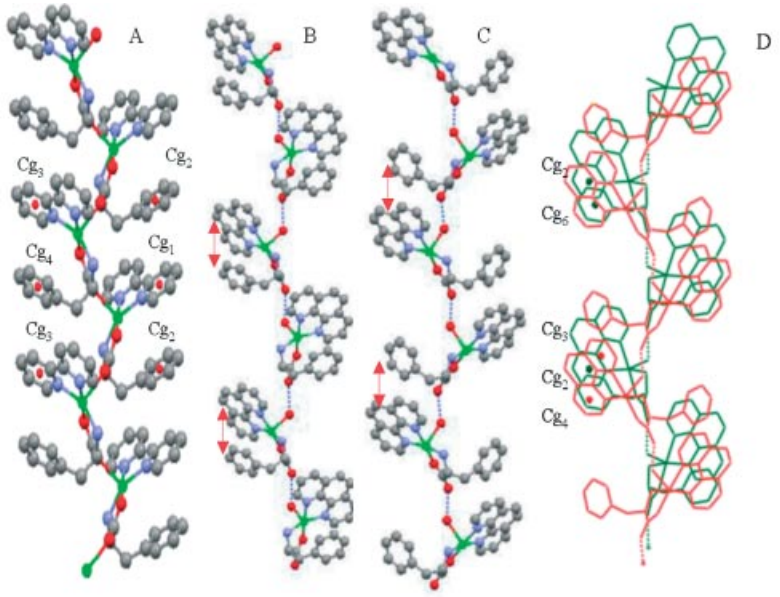


Figure 2. Stacking interactions of the phenyl rings in complexes **1** and **2** along the *a* axis. The double-headed arrows indicate the inter- and intramolecular stacking interactions. A: complex **1** [inter: Cg(1)···Cg(2) 4.158 Å; intra: Cg(1)···Cg(2) 4.154 Å; inter: Cg(3)···Cg(4) 4.264 Å; intra: Cg(3)···Cg(4) 4.044 Å]; B: complex **2** (only folded form); C: complex **2** (only extended form); D: merged packing of **2a** and **2b** [intra: Cg(2)···Cg(6) 3.882 Å; inter: Cg(3)···Cg(2) 3.539 Å]. Color scheme: red = carboxylate oxygen; green = Cu(II).

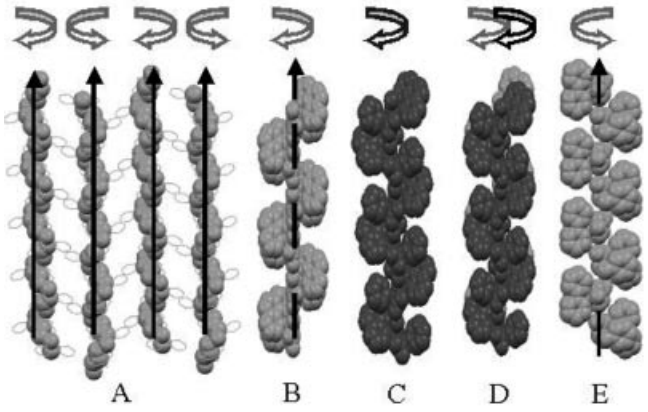


Figure 3. Space-filling model of the single-stranded supramolecular helical arrangements formed by Cu–OCO–Cu connectivity (light gray = folded; dark gray = extended). A: **1**; B: **2a**, C:**2b**; D: addition of both **2a** and **2b**; E: **3**.

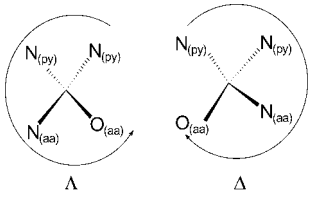
through hydrogen bonding to create another helical chain. An alternate arrangement of O–H···O interactions with the lattice water molecule O3w and N–H···O bonds brings the adjacent folded and extended helical chains into close proximity to create a sheet-like architecture that restores the helical superstructure of the complex. The combined effect of various O–H···O and N–H···O interactions involving O3w–O2 (2.742 Å), O3w···O2w (2.745 Å), and N(3)H···O4 (3.024 Å) and π···π stacking interactions brings the Cu^{II} centers into closer contact (5.928 Å). The hydrogen-bonded helical superstructure formed by both the folded and extended isomers can be designated as (*P*) because of the clockwise sense of its molecular rotation, as shown in Figure 3D. The folded and extended forms are shown separately in Figures 3B and C to better visualize their similar helical chirality.

Supramolecular helices usually pack in a racemic fashion,[19] and reports on homochiral helicates are rare. Supramolecular packing of **1**, for instance, occurs with the usual racemic pattern comprising both the (*P*) and (*M*) alternate helical chains, while in the crystal structure of complex **2** packing of two (*P*) helices occurs stereospecifically to give a homochiral superstructure, as shown in Figures 3B–D. In complex **3**, the free carboxylate oxygen atom (O2) involved in N···H···O interactions [N(3)–H···O2 3.027 Å] forms a single-stranded inner-sphere helical chain through the Cu1–N3···O2CO1–Cu1 bonds along the *bc* plane, as shown in Figure 3E.

Chiroptical Properties

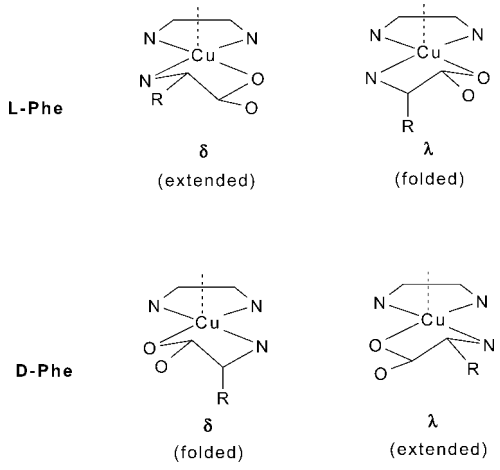
In order to understand the correlation between the supramolecular helical architecture and the chiroptical properties, CD spectra for complexes **1**–**3** were recorded both in solution and on ground crystals. In general, the optical activity could be derived from the (*P*)/(*M*) helical chain chiral descriptors, the geometrical Δ/Λ descriptors of the chiral metal centers (Scheme 1), and the λ/δ conformational chirality[20] of the nonplanar L/D-amino acid chelate rings. For systems **1**–**3**, therefore, an attempt to correlate their chiroptical properties can be made. Chirality at the metal centers can be derived by taking into account the non-coplanar arrangement of the donor atoms at the base of the square pyramid in the structures of the Cu^{II} centers; the descriptors[21] Δ and Λ are thus assigned depending upon the clockwise (Δ isomer) and anticlockwise (Λ isomer) operation of the chromophore $O_{(aa)} \rightarrow N_{(aa)} \rightarrow N_{(py)}$

→ $N_{(py)}$ around the Cu^{II} center, as shown in Scheme 1. In complex **1**, the (*P*) sense of the helix is associated with ΔΔΔΔ... configurations at the metal centers, while the (*M*) sense involves ΛΛΛΛ... configurations at the Cu atoms. The amino acids in complex **2** exist in folded (**2a**) and extended (**2b**) forms, both of which selectively assemble into (*P*) helical chains, although the configuration at the metal centers is ΛΔΛΔ... in the skeleton of the two helices. Furthermore, as complexes **1** and **2** possess very similar chemical compositions, the difference in their spatial arrangement caused by the folded and extended isomer and the extra space provided by the phenanthroline ligand may be the reason for its homochiral nature.



Scheme 1. Geometrical descriptors.

As regards the conformation of the amino acid chelate rings, it should be noted that the folded isomer has λ chirality for the L-phe and δ chirality for the D-phe residues, and that the opposite chirality occurs for the corresponding extended isomers (Scheme 2). The amino acids in the helical chains of complexes **1** and **3** adopt the folded conformation (λ for L-phe and δ for D-phe), although both the folded D-phe residue in **2a** and the extended L-phe residue in **2b** bear the same δ chirality.



Scheme 2. Conformations of the amino acid chelate rings.

Complex **1** assembles in alternating (*P*) and (*M*) helices through Cu1–OCO–Cu2 chains, therefore both the contributions to the overall chirality by the conformation of the amino acid chelate rings and the configuration at the Cu^{II} centers perfectly cancel each other out in the enantiomeric (*P*) and (*M*) helices. In contrast, the two supramolecular helical chains built up by the D- and L-phe complexes in complex **2** bear the same (*P*) chirality. This shows that the chirality of the helical chain is dictated by the conformational chirality of the amino acid chelate ring rather than the absolute (L/D) configuration of the amino acid, with a λ conformation inducing an (*M*) helix and a δ conformation a (*P*) helix. The self-assembly process generating the helical chains is thus enantioselectively dictated by the folded or extended disposition assumed by the side-chain of the phe residues.

As expected, the CD spectra of complexes **1** and **2** in solution are flat as the polymeric structure is destroyed; the solid-state CD spectrum of complex **1** is also essentially flat, taking into account the low resolution of the experiment, whereas crystals of complex **2** appear to exhibit optical activity in the solid state, with weak but clearly detectable CD activity with a positive sign between 500 and 600 nm. The dominant CD activity for complex **3** has a negative sign and remains unchanged both in the solid state ($\lambda_{max} \approx$ 620 nm) and in solution [CD data in methanol: $\lambda_{max} \approx 565$ ($\Delta\varepsilon = -0.44\ M^{-1}\,cm^{-1}$) and 725 nm (+0.10)], thus clearly indicating that no significant change occurs in the chiral arrangement of the complex. The CD activity observed for complexes **2** and **3** in the Cu^{II} d-d bands therefore reflects the opposite chirality of the amino acid chelate rings and of the corresponding helical chains associated with the two complexes in the crystalline state.

Conclusion

We have described the formation of a series of single-stranded helical coordination polymers that contain both covalent and hydrogen bonds as a construction element. The two separate helical chains of the ternary complex carrying L- and D-phe residues in complex **1** bear opposite chirality, which means that the crystalline sample as a whole is racemic. In contrast, the two helical chains generated by the L- and D-phe complexes in **2** have the same (*P*) chirality and together form two right-handed helical assemblies. In principle, a supramolecular arrangement involving two helical chains with (*M*) chirality, built from the folded (L) and extended (D) forms of the racemic amino acid, is possible for this complex, but is probably not observed in the crystalline state due to the less favorable packing. Further studies on chiral amplification to monitor the crystallization process of metal complexes containing optically pure and racemic amino acids are currently under way in our laboratory.

Experimental Section

Materials: L-Phenylalanine, D,L-phenylalanine, 2,2′-bipyridyl, and 1,10-phenanthroline were purchased from Sigma–Aldrich and used as received. All the other reagents and solvents were commercially available and used without further purification. Microanalysis of the complexes was performed with a Perkin–Elmer PE 2400 series II CHNS/O elemental analyzer. FT-IR spectra for KBr pellets (1% w/w) were recorded with a Schimadzu FT-COM 1 spectrophotometer. The CD spectra were measured for KBr pellets or methanol solutions of the complexes with a JASCO J710 dichrograph; a smoothing program from JASCO (version 1.53.00) was used to reduce the noise of the solid-state spectra.

Table 2. Summary of the crystallographic parameters for complexes **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{38}H_{36}Cl_2Cu_2N_6O_{12}$	$C_{42}H_{42}Cl_2Cu_2N_6O_{15}$	$C_{19}H_{20}ClCuN_3O_7$
Formula mass	966.71	1068.80	501.37
Crystal size [mm]	$0.45\times0.20\times0.08$	$0.35\times0.20\times0.10$	$0.36\times0.26\times0.24$
Crystal description	plates	plates	blocks
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1$
a [Å]	8.3033(8)	13.3582(10)	7.2743(7)
b [Å]	13.7280(13)	25.3803(18)	11.3581(10)
c [Å]	18.2520(18)	14.1334(10)	12.5857(11)
α [°]	68.282(2)	90.00	90.00
β [°]	84.708(2)	113.775(10)	102.845(2)
γ [°]	82.050(2)	90	90
Volume [Å^3]	1912.3(3)	4385.1(5)	1013.84(16)
Z	2	4	2
$D_{calcd.}$ [g cm^{-3}]	1.679	1.619	1.642
$F(000)$	988	2192	514
μ (Mo-K_α) [mm^{-1}]	1.326	1.170	1.258
Temperature [K]	293(2)	293(2)	293(2)
2θ max	22.50	28.24	28.27
Observed reflections [$I > 2\sigma(I)$]	4930	10159	3636
Parameters refined	541	756	352
Goodness of fit	1.054	1.050	1.054
Final R_1 (observed data)	0.0435	0.0441	0.0222
Final wR_2 (observed data)	0.1263	0.1270	0.0581

Preparation of the Complexes

[Cu(D,L-phe)(bpy)]·ClO$_4$ (1): A mixture of D,L-phenylalanine (0.82 g, 10 mmol) and NaOH (0.20 g, 10 mmol) in distilled water (50 mL) was added to an aqueous solution (25 mL) of $CuSO_4{\cdot}5H_2O$ (1.25 g, 10 mmol) and stirred for 30 min. The solution was stirred at 50 °C for another 2 h until a pale-blue precipitate had formed. An ethanolic solution (20 mL) of bipyridyl (0.78 g) was then added dropwise and the pale-blue precipitate was observed to dissolve to form a clear blue solution. At the end of the reaction, $NaClO_4{\cdot}H_2O$ (0.7 g, 10 mmol), dissolved in distilled water (20 mL), was added. $C_{19}H_{18}ClCuN_3O_6$ (483.36): calcd. C 47.30, H 3.73, N 8.71; found C 47.35, H 3.76, N 8.63. IR: $\tilde{\nu}$ = 3450–2910, 1631, 1593 (s), 1444, 1386 (m), 1320 (m), 1131, 1103, 1057 (br., s), 763, 618 (m) cm^{-1}.

[Cu(D,L-phe)(phen)(H$_2$O)]·ClO$_4$·H$_2$O (2): This complex was synthesized according to the above procedure but with phenanthroline (0.94 g, 10 mmol) in place of bipyridyl. $C_{21}H_{21}ClCuN_3O_{7.5}$ (530.40): calcd. C 47.19, H 3.96, N 7.86; found C 47.42, H 4.54, N 7.27. IR: $\tilde{\nu}$ = 3519–2940 (br., s), 1609, 1589 (ν_{COO}, s), 1520 (m), 1429, 1399 (m), 1149, 1100, 1085 (ν_{ClO_4}, br, s), 851 (m), 622 (m) cm^{-1}.

[Cu(L-phe)(bpy)(H$_2$O)]·ClO$_4$·H$_2$O (3): Synthesized and characterized according to the reported procedure.[9]

Crystal Structure Determination: Data collection for **1**–**3** was performed with a Bruker Apex CCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å) at 100(2) K. Absorption corrections were applied with the multi-scan program SADABS.[22a] Further details are given in Table 2. The structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the program SHELXTL.[22b] Hydrogen atoms were generated with a riding model. CCDC-281899 (**1**), -281900 (**2**), and -281901 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Table summarizing hydrogen-bonding network for complexes **1** and **2**.

Acknowledgments

P. S. and E. S. are grateful to Dr. P. K. Ghosh, Director of the Central Salt and Marine Chemicals Research Institute, for his keen interest and encouragement, and Dr. A. Granata for recording the CD spectra.

[1] a) S. G. Telfer, T. Sato, R. Kuroda, *Angew. Chem.* **2004**, *116*, 591; *Angew. Chem. Int. Ed.* **2004**, *43*, 581; b) M. Ziegler, A. V. Davis, D. W. Johnson, K. N. Raymond, *Angew. Chem.* **2003**, *115*, 689; *Angew. Chem. Int. Ed.* **2003**, *42*, 665; c) G. Tian, G. Zhu, X. Yang, Q. Fang, M. Xue, J. Sun, Y. Wei, S. Qin, *Chem. Commun.* **2005**, 1396; d) X.-M. Chen, G.-F. Liu, *Chem. Eur. J.* **2002**, *8*, 4811; e) M. Suareez, N. Branda, J.-M. Lehn, A. Decian, J. Fischer, *Helv. Chim. Acta* **1998**, *81*, 1; f) E. Yashima, K. Maeda, T. Nishimura, *Chem. Eur. J.* **2004**, *10*, 42.

[2] a) O. Yamauchi, A. Odani, M. Takani, *J. Chem. Soc., Dalton Trans.* **2002**, 3411; b) O. Yamauchi, A. Odani, *J. Am. Chem. Soc.* **1981**, *103*, 391; c) O. Yamauchi, A. Odani, T. Kohzuma, H. Masuda, K. Toriumi, K. Saito, *Inorg. Chem.* **1989**, *28*, 4066; d) F. Zhang, A. Odani, H. Masuda, O. Yamauchi, *Inorg. Chem.* **1996**, *35*, 7148; e) O. Yamauchi, A. Odani, *J. Am. Chem. Soc.* **1985**, *107*, 5938.

[3] a) J. Pasan, J. Sanchiz, C. Ruiz-Perez, F. Lloret, M. Julve, *Eur. J. Inorg. Chem.* **2004**, 4081; b) T. Kahzuma, H. Masuda, O. Yamauchi, *J. Am. Chem. Soc.* **1989**, *111*, 3431.

[4] a) H. Sigel, R. Malini-Balakrishnan, U. K. Haring, *J. Am. Chem. Soc.* **1985**, *107*, 5137; b) E. Dubler, U. K. Haring, K. H. Scheller, P. Sigel, *Inorg. Chem.* **1984**, *23*, 3785; c) A. Castineiras, A. G. Sicilia-Zafra, J. M. Gonzalez-Perez, D. Choquesillo-Lazarte, J. Niclos-Gutierrez, *Inorg. Chem.* **2002**, *41*, 6956.

[5] a) S. Suzuki, K. Yamaguchi, N. Nakamura, Y. Tagawa, H. Kuma, T. Kawamoto, *Inorg. Chim. Acta* **1998**, *283*, 260; b) U. Mukhopadhyay, D. Choquesillo-Lazarte, J. Niclos-Gutierrez,

I. Bernal, *Cryst. Eng. Commun.* **2004**, *6*, 627; c) F. Zhang, T. Yajima, H. Masuda, A. Odani, O. Yamauchi, *Inorg. Chem.* **1997**, *36*, 5777; d) L. H. Abdel-Rahman, L. P. Battaglia, M. R. Mahmoud, *Polyhedron* **1996**, *15*, 327.

[6] a) N. Nakamura, T. Kohzuma, H. Kuma, S. Suzuki, *J. Am. Chem. Soc.* **1992**, *114*, 6550; b) . J. L. Seymour, F. Turecek, A. V. Malkov, P. Kocovsky, *J. Mass. Spectrom.* **2004**, *39*, 1044.

[7] M. Mizutani, S. Tomosue, H. Kinoshita, K. Jitsukawa, H. Masuda, H. Einaga, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 981.

[8] T. Sugimori, H. Masuda, N. Ohata, K. Koiwai, A. Odani, O. Yamauchi, *Inorg. Chem.* **1997**, *36*, 576.

[9] P. S. Subramanian, E. Suresh, P. Dastidar, S. Waghmode, D. Srinivas, *Inorg. Chem.* **2001**, *40*, 4291.

[10] a) V. G. Machado, P. N. W. Baxter, J.-M. Lehn, *J. Braz. Chem. Soc.* **2001**, *12*, 431; b) J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier, D. Moras, *Proc. Natl. Acad. Sci. USA* **1987**, *84*, 2565; c) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005.

[11] a) R. Prabaharan, N. C. Fletcher, M. Nieuwenhuyzen, *J. Chem. Soc., Dalton Trans.* **2002**, 602; b) Y.-T. Way, M.-L. Tong, H.-H. Fan, H.-Z. Wang, X.-M. Chen, *Dalton Trans.* **2005**, 424.

[12] L. J. Prins, P. Timmerman, D. N. Reinhoudt, *J. Am. Chem. Soc.* **2001**, *123*, 10153.

[13] a) C. J. Carrano, K. N. Raymond, *J. Am. Chem. Soc.* **1978**, *100*, 5371; b) A.-K. Duhme, Z. Dauter, R. C. Hider, S. Pohl, *Inorg. Chem.* **1996**, *35*, 3059.

[14] a) M. Duggeli, C. Goujon-Ginglinger, S. R. Ducotterd, D. Mauron, C. Bonte, A. V. Zelewsky, H. Stoeckli-Evans, A. Neels, *Org. Biomol. Chem.* **2003**, *1*, 1894; b) O. Mamula, A. V. Zelewsky, T. Bark, G. Bernardinelli, *Angew. Chem.* **1999**, *111*, 3129; *Angew. Chem. Int. Ed.* **1999**, *38*, 2945; c) O. Mamula, F. J. Monlien, A. Porquet, G. Hopfgartner, A. E. Merbach, A. V. Zelewsky, *Chem. Eur. J.* **2001**, *7*, 533; d) A. V. Zelewsky, *Coord. Chem. Rev.* **1999**, *190–192*, 811.

[15] a) M. Meyer, B. Kersting, R. E. Powers, K. N. Raymond, *Inorg. Chem.* **1997**, *36*, 5179; b) B. Kresting, M. Meyer, R. E. Powers, K. N. Raymond, *J. Am. Chem. Soc.* **1996**, *118*, 7221; c) D. Caulder, K. N. Raymond, *J. Chem. Soc., Dalton Trans.* **1999**, 1185; d) J. Xu, T. N. Parac, K. N. Raymond, *Angew. Chem.* **1999**, *111*, 3055; *Angew. Chem. Int. Ed.* **1999**, *38*, 2878.

[16] a) M. Albrecht, O. Spieß, M. Schneider, P. Weis, *Chem. Commun.* **2002**, 786; b) M. Albrecht, M. Napp, M. Schneider, P. Weis, R. Frohlich, *Chem. Eur. J.* **2001**, *7*, 3966; c) M. Albrecht, M. Napp, M. Schneider, P. Weis, R. Fröhlich, *Chem. Commun.* **2001**, 409.

[17] a) S. J. Telfer, R. Kuroda, *Chem. Eur. J.* **2005**, *11*, 57.

[18] K. Akoi, H. Yamazaki, *J. Chem. Soc., Dalton Trans.* **1987**, 2017.

[19] J. Breu, H. Domel, A. Stoll, *Eur. J. Inorg. Chem.* **2000**, 2401.

[20] L. Casella, M. Gullotti, *J. Am. Chem. Soc.* **1981**, *103*, 6338.

[21] a) L.-S. Long, J.-W. Cai, Y.-P. Ren, Y.-X. Tong, X.-M. Chen, L.-N. Ji, R.-B. Huang, L.-S. Zheng, *J. Chem. Soc., Dalton Trans.* **2001**, 845; b) H. Miyasaka, S. Okamura, T. Nakashima, N. Matsumoto, *Inorg. Chem.* **1997**, *36*, 4329.

[22] a) G. M. Sheldrick, *SADABS 2.05*, University of Göttingen, Germany; b) *SHELXTL 6.10*, Bruker Analytical Instrumentation, Madison, WI, **2000**.

Received: October 13, 2006
Published Online: March 6, 2007

